MINERALOGICAL AND CHEMICAL CHARACTERISTICS OF PHOSPHATES IN SOME FLORIDA PHOSPHATIC SOILS

BY

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To my beloved motherland.

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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

MINERALOGICAL AND CHEMICAL CHARACTERISTICS OF PHOSPHATES IN FLORIDA PHOSPHATIC SOILS

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Twelve Florida virgin soil pedons (phosphatic) with > 7 g/kg total P in B or C horizons were investigated to establish the relationship between phosphate mineralogy and soil properties. Wavellite [$Al_3(PO_4)_2(OH)_3.5H_2O$] was found in all the Ultisols and one Alfisol. Carbonate-fluorapatite [$Ca_{10}(PO_4,CO_3)_6F_{2-3}$] and crandallite [$CaAl_3(PO_4)_2(OH)_5.H_2O$] were restricted to horizons with relatively low eluviation, high base saturation, high extractable-Ca, low KCl-extractable Al, and poorly- to somewhat-poorly-drained conditions.

Noncrystalline P was indicated by insufficient mineral-P to account for total-P. Mineral-P/total-P ratio was lower in A and E horizons compared to Btg2 and C horizons. Noncrystalline P was more extractable by oxalate, Mehlich I, and Olsen extractants than was mineral-P.

The effect of P on Fe crystallinity and extractability was studied using profiles of nine soils with more than 200 mmol/kg Dithionite-citrate-bicarbonate (DCB)-extractable Fe. Goethite was detected in all the soils low in total P (< 33 mmol/kg); however, neither crystalline Fe-P nor Fe oxides were detected by XRD in the soils high in total P (>176 mmol/kg). The presence of high P in soils apparently interfered with Fe crystallization.

Effects of dilute organic acids on carbonate-fluorapatite and wavellite dissolution were studied by laboratory incubation with two concentrations of formic, oxalic, and citric acids which provided $3x10^{-2}$ and $3x10^{-3}$ M carboxyl groups, respectively. Soluble P from carbonate-fluorapatite and wavellite increased with organic acid concentrations but decreased in the order, oxalic > citric > formic > water. The presence of common clay minerals decreased soluble P by organic acids.

The P minerals and phosphatic soils containing 20 mg P were extracted for P with DCB. The DCB extracted all Fe-P and large amounts of Fe-Al-P and noncrystalline Al-P; but little P from wavellite, variscite, crandallite, and carbonate-fluorapatite.

CHAPTER 1
INTRODUCTION

Marine phosphate deposits are widely distributed in Florida (Florida Defenders of the Environment, 1984). The phosphate deposits include land pebble deposits and hard rock deposits (Cathcart, 1980).

Altschuler et al. (1956) showed that phosphate deposits of the Bone Valley formation of Pliocene age overlay the Hawthorn formation of early to middle Miocene age and was covered by a surface mantle of quartz sands called overburden. Generally, soils (0 to 2 m depth) above phosphate mines contain little P because their parent materials were residual sand possibly of Pleistocene age (Altschuler, 1956; United States Environmental Protection Agency, 1978). However, phosphatic pebbles have been found in some soils within two-meter depth in Marion (Carlisle et al., 1978), Alachua (Carlisle et al., 1981), Union and DeSoto counties (Carlisle et al., unpublished). The phosphatic pebbles range from 2 to 75 mm in size and occupy up to about 15% of soil volume in certain horizons of soil profiles. Total P content in the subhorizon of some of these soils is as high as 34.8 g P/kg. In Sumter, Madison, DeSoto,

and Polk Counties, some soil series may contain from 4 to 20 g P/kg, although pebbles were not found.

The phosphatic soils in Florida include Ultisols, Alfisols, Entisols, Inceptisols, and Spodosols. Most of these soils are acidic, ranging from pH 4.2 to 6.5. Topography, slope and water tables vary from soil to soil. Most areas are forested, but some are used for pasture or crops. Organic matter content decreases with depth and varies from soil to soil. Significant concentrations of organic acids produced by microbiological activity can be present in surface and near surface soil horizons (Hue et al., 1986; Earl et al., 1979). These soil and environmental factors may affect the weathering and formation of phosphate minerals; and there may be a relationship between soil properties and the species of phosphate minerals present. The relationships are poorly understood and warrant further study.

The land-pebble phosphates of the Bone Valley Formation are in well crystalline forms, and noncrystalline P has not been reported. In the soils, P can also be retained by clay minerals and Al- and Fe-oxides and hydroxides in addition to phosphate minerals (Tisdale et al., 1985). The direct determination of phosphate minerals in soils is very difficult due to low total P (Lindsay and Vlek, 1977); but it is possible in phosphatic soils due to much higher total P content. The ratio of crystalline P/total P in these soils

can reflect the portion of noncrystalline P, which can be related to the soil properties.

Soil properties in the phosphatic soils may be affected by P due to high total phosphate content. For example, P has been reported to restrict goethite formation (Schwertmann and Taylor, 1977). In the soil system, the effect of phosphate on Fe crystallization has not been reported.

Therefore, the objectives of this study include the following:

1. To determine the phosphate minerals in selected phosphatic soils and to relate their stability to the soil chemical and mineralogical properties.

2. To determine the extent and forms of noncrystalline P present in selected phosphatic soils.

3. To study the relationship between P and Fe in selected phosphatic soils, and to examine evidence of a restricting effect of P on Fe crystallization.

4. To determine the effects of organic acids on P-mineral dissolution, and consider the implications for P availability to plants.

5. To determine the effectiveness of sequential P-fractionation schemes in partitioning P-mineral forms using soils and standard minerals.

CHAPTER 2
LITERATURE REVIEW

2.1. Formation and Distribution of Phosphorite in Florida

Phosphorite of the Miocene in Florida was formed from marine deposits. Deep cold P-rich ocean water was the source of the P in phosphorite (Kazakov, 1938, Riggs, 1979). Kazakov (1938) suggested that the deep ocean water ascended into the shallow photic zone. Apatite directly precipitated from the ascending water column, then accumulated as phosphate grains on the shelf. However, Riggs (1979) suggested that phosphorite after precipitation was altered by biological and physical processes and then transported off the shoals by periodic high-energy conditions until they were deposited and accumulated in the adjacent entrapment basins and on the flanks of the structural highs.

The Bone Valley discontinuously overlies the Hawthorn formation of early and middle Miocene age (MacNeil, 1947; Altschuler et al., 1956) and is covered by a mantle of loose quartz sand of Pleistocene.

Phosphate deposits in Florida include land-pebble and hardrock-phosphate deposits (Forida Defenders of the Environment, 1984). The land-pebble deposits occur in central and south Florida, northern Florida, and eastern

Florida. The hardrock-phosphate deposits occur along a narrow elongated band in Hernando, Citrus, Levy, Marion, and Gilchrist counties. The hardrock phosphate deposits were formed when P, dissolved by acid ground water, moved downward and was precipitated on or replaced underlying limestone (Cathcart, 1980). Hardrock phosphate is characterized by large boulders, pebbles, and plates of phosphate and/or phosphatized limestone mixed with material of smaller size.

A typical stratigraphic section, in central Florida, consists of a top soil zone, an overburden zone, a leached zone, a matrix zone, a bedclay zone, and a bedrock zone (Cathcart, 1956; United States Environmental Protection Agency, 1978).

In the top soil zone and overburden zone, quartz sand and kaolinite are the predominant minerals, and phosphate minerals are uncommon. Phosphate deposits occur dominantly in the leached zone and matrix zone and decrease in the bedclay zone. Phosphorite in the leached zone has been altered by weathering processes to form secondary minerals such as wavellite, crandallite, and millisite; while in the matrix zone, phosphorite has been well preserved (Altschuler et al., 1964; United States Environmental Protection Agency, 1978).

2.2. Weathering of Phosphate Minerals and the Affecting Factors

The weathering of marine primary apatite results in a loss of CO_2 from the structure and an increase of the unit cell parameter [a] (McClellan and Lehr, 1969; Altschuler, 1973). Calcium from apatite is removed when the environment becomes acidic and depleted in Ca. New minerals appear in the intense weathering stage. At the top of the weathering zone, Fe phosphates such as rockbridgeite $[Fe^{+2}Fe^{+3}_4(PO_4)_3(OH)_5]$ (Blanchard, 1969), cacoxenite $[(Fe^{+3},Al)_{25}(PO_4)_{17}O_6(OH)_{12}.17H_2O]$ and Beraunite $[Fe^{2+}Fe^{3+}_5(PO_4)_4(OH)_5.4H_2O$ (Blanchard and Denahan, 1968) and aluminum phosphates such as variscite $[AlPO_4.2H_2O]$ (Blanchard and Denahan, 1966) and wavellite $[Al_3(PO_4)_2(OH)_3.5H_2O]$ (Altschuler et al., 1956) form; while at the bottom and in the substratum secondary apatites develop (Altschuler et al., 1956).

Most of the Fe and Al phosphates are unstable and undergo progressive alteration with continued weathering. Several tendencies are observed: change to greater hydration, change to higher Al-Fe/P ratios, and in the case of Fe phosphates, a change to higher oxidation state (Altschuler, 1973; Flicoteaux and Lucas, 1984).
The stable phases are crandallite and millisite if alkalis are present, and wavellite and augelite $[Al_2PO_4(OH)_3]$ without alkalis. Augelite appears to form only with intense or long-

term leaching (Altschuler, 1973). The replacement of phosphorite by secondary phosphates may be derived from two directions, namely, phosphatization of clay or the attack of Al-bearing solutions on apatite.

During the process of phosphorite weathering, montmorillonite and illite are also transformed to kaolinite. Vieillard et al. (1979) observed the distribution of phosphate minerals and clay minerals on lateritic weathering profiles from the bottom to the top in the sequence: carbonate-fluorapatite + montmorillonite + calcite → carbonate-fluorapatite + montmorillonite → carbonate-fluorapatite + kaolinite → crandallite + kaolinite → wavellite + kaolinite → augelite → gibbsite.

The rate of chemical breakdown of phosphate rock particles relates to chemical and mineralogical differences of phosphate rocks, apatite crystal size, apatite solubility (Khasawneh and Doll, 1978) and rock particle size (Joos and Black, 1950; Caro and Hill, 1956; Armiger and Fried, 1958). The parent rock porosity or density also controls the rate of leaching. Reactivity decreases with increasing compactness (Caro and Hill, 1956). This factor can explain how wavellite constitutes the most frequent mineral in Florida phosphorites, in which Ca phosphate nodules are scattered in a porous quartzous material, while crandallite dominates in the deposits of Togo and western Senegal which contain less quartzous material (Flicoteaux and Lucas,

1984). The paragenetic sequences vary depending on the geochemical nature of the parent rock. In Fe-deficient rocks a highly aluminous taranakite may form and be succeeded by variscite (Altschuler et al., 1973).

Several soil factors that influence phosphate rock dissolution have been identified. These include soil pH (Joos and Black, 1950; Graham, 1955; Khasawneh and Doll, 1978; Mackay and Syers, 1986); soil pH-buffering capacity or power (Graham, 1955); exchangeable Al (Chien, et al., 1980) and Ca (Graham, 1955; McLean and Balam, 1967; Mackay and Syers, 1986); soil solution P concentration (Van Der Paauw, 1965); and soil P fixation (McLean and Balam, 1967) and P buffering capacities (Chu, et al., 1962; Van Der Paauw, 1965). The rate of apatite dissolution increases with increasing soil acidity and acid buffering power (Anderson et al., 1985). Apatite solubility is strongly influenced by activities of reaction products in the surrounding soil solution (Chien, 1977; Wier et al., 1971). Therefore, the change in soil solution activities of Ca^{+2}, HPO_4^{-2}, and $H_2PO_4^-$ ions, as well as in soil P buffer power and exchangeable Ca will affect apatite dissolution.

The nature of secondary phosphate minerals may be affected by ground water. Reactions of decarbonated groundwater with layer silicates and Ca phosphates can produce millisite, crandallite, wavellite, and perhaps augelite $Al_2PO_4(OH)_3$ (Flicoteaux and Lucas, 1984). Sodium may

be depleted under highly leaching conditions and millisite may not form with crandallite (Altschuler et al., 1956).

The topographic relief regulates drainage and any changes in relief over time may induce changes in the nature or concentration of percolating solutions (Flicoteaux and Lucas, 1984).

2.3. Forms of P in Soils

Soil P can be classed generally as organic and inorganic. The inorganic fraction of soil P occurs in numerous combinations with Fe, Al, Ca, F, and other elements as well as in insoluble clay-phosphate complexes (Tisdale et al., 1985). These inorganic P forms may be crystalline, adsorbed (Lindsay and Vlek, 1977), and noncrystalline.

Crystalline or noncrystalline mineral P may form by precipitation-dissolution reactions. Most initial precipitates of Fe and Al phosphates are noncrystalline and show solubilities that are 10 to 100 times greater than the crystalline minerals (Haynes, 1982). The sorbed P may also be present (Sanchez and Uehara, 1980; Tisdale et al., 1985). Phosphate precipitation occurs only at high solution-P concentrations. At low P concentrations, adsorption seems to be the dominant mechanism (Tisdale et al., 1985).

Phosphate minerals formed in soils are frequently not pure Al or pure Fe phosphates (Tan, 1982). A series of intergrades between variscite and strengite is usually present in soils and is called the variscite-strengite solid

solution (Lindsay et al., 1959). These products are sparingly soluble although with a higher solubility product than variscite (Lindsay et al., 1962; Bache, 1964).

The adsorbed P accounts for P retained on soil particle surfaces. The surfaces retaining phosphate ions are of two main types, constant charge and constant potential surfaces (Bohn et al., 1979; Gast, 1977). The surfaces of constant charge, such as the 2:1 type crystalline clay minerals, are produced from either structural imperfections in the interior of the crystal structure or preferential adsorption of certain ions on particle surfaces (van Olphen, 1963). The constant charge surfaces interact with P principally through the polyvalent cations held tightly to their platelike surfaces, such as Al, Fe, and Ca (Tisdale et al., 1985). The second category involves surfaces of variable charge including the Fe (III) and Al oxides and organic matter. These oxides can absorb water and form hydroxylated surface, and charge can develop on these hydroxylated surfaces either through amphoteric dissociation of the surface hydroxyl groups or by adsorption of H^+ or OH^- ions to form positive or negative charges according to the acid strength and ambient pH (Gast, 1977).

Some clay minerals such as kaolinite have pH-dependent charges on their crystal edges. Noncrystalline clay minerals such as allophane are amphoteric, having either negative, zero, or positive charge, depending on the pH. The pH at

which the net charge on the surface is zero is defined as the zero point of charge (ZPC) (Parks, 1962; Gast, 1977). Aluminum and Fe on oxides have respective ZPC of approximately 8.5 and 9; and the edge surfaces of kaolinite have a ZPC of about 7 (Tisdale et al., 1985). At pH levels below the ZPC, phosphorus ions are attracted to the positively charged oxide surface. Further, organic matter, with a pH-dependent charge surface, reacts with P through its cations held by coulombic forces (Tisdale et al., 1985). In soils with significant contents of Fe and Al oxides, the P retention capacity decreases with increasing crystallinity of Fe and Al oxides because of reducing specific surface area (Colwell, 1959; Fox et al,. 1971). Crystalline hydrous metal oxides are usually capable of retaining more P than layer silicates. Phosphorus is retained to a greater extent by 1:1 than by 2:1 clays. This is more than likely due to the amounts of hydrated oxides of Fe and Al associated with kaolinitic clay as well as their edge-associated pH-dependent charge of kaolinite (Sanchez and Uehara, 1980). Concentrations of exchangeable Al (Coleman et al., 1960; Larsen et al., 1959), Fe (Larsen et al., 1959), and Ca (Calvert et al., 1960; Ragland and Seay, 1957) are also important factors in P retention in soils.

2.4. Interaction between P and Fe

Iron phosphates are less common than Al phosphates. Acid meteoric waters lead to the generation of Fe phosphates only in the absence of clayey material, or in very reducing conditions. In Florida deposits, goethite is the principal Fe mineral. Goethite can be precipitated from downward-moving humate-rich groundwater in zones of concretions and hardpans in the lateritized phosphates (Altschuler, 1973). Due to interaction with phosphatic solutions these secondary Fe deposits may be partly replaced by vivianite [$Fe_3(PO_4)_2.8H_2O$] concretions, and by beraunite and cacoxenite (Blanchard and Denahan, 1968; Altschuler, 1973). Both ferric and Al phosphates are stable relative to apatite under conditions of acid alteration; however, Fe phosphates are not common and are volumetrically unimportant in sedimentary phosphates compared to the ubiquitous Al phosphates (Altschuler, 1973). The formation of Fe phosphates may be due to the prominence of humic accumulations in the soils of highly humid regions and to the reducing effects of organic acids in water (Altschuler, 1973). Sah and Mikkelsen (1986) concluded that the anaerobic decomposition of organic matter increased the transformation of crystalline Fe into noncrystalline Fe, decreased the Al-P, and increased the Fe-P and reductant-soluble P fractions.

2.5. Effect of Organic Acids on Phosphate Solubility

The effect of organic acids on phosphate mineral dissolution has not been extensively studied. Organic acids can probably dissolve phosphate minerals through forming complexes between organic acid and cations such as Al (Kwong and Huang, 1979). Goh and Huang (1984) and Traina et al. (1986) showed that organic acids at low concentrations acted principally to increase the quantity of exchangeable Al^{+3} through displacement of hydroxyl ions from adsorbed Al-OH by ligand exchange, thereby enhancing the potential for Al to react with o-phosphate. However, at higher concentrations organic acids act principally to decrease the quantity of exchangeable Al^{+3} in favor of soluble complexes that do not react with o-phosphate to reduce its solubility. Two types of competing reactions between organic acids and the Al^{+3} ion have been summarized by Traina et al. (1986). The first was the reaction of adsorbed, polymeric hydroxy-Al with organic ligand to form an exchangeable Al species which combined with o-phosphate to reduce its solubility; the second was the complexation of adsorbed Al to form a soluble Al-organic complex that did not subsequently combine with o-phosphate.

2.6. Selective Extractability of Phosphates

Characterization of the forms of inorganic phosphate in soils was studied by Fraps (1906), and was developed by Fisher and Thomas (1935), Williams (1937), Dean (1938), and

Williams (1950). In their studies Fe- and Al-P were combined into the same fraction. Turner and Rice (1952) found that neutral ammonium fluoride can dissolve aluminum phosphate but not Fe phosphate. Ammonium fluoride was subsequently introduced (Chang and Jackson, 1957) to distinguish between Al- and Fe-bound P. In their fractionation scheme, Chang and Jackson (1957) assumed that NH_4F-P originated predominantly from Al phosphates, such as variscite and wavellite, or from phosphate bonded to Al-rich components, such as allophane. The subsequent NaOH-P was believed to originate from Fe phosphates, such as strengite, or "nonoccluded" phosphate bonded by sorption reactions to the surfaces of Fe-rich minerals such as hydrated Fe oxides. The "reductant-soluble P" fraction originated from phosphate occluded within the matrices of hydrated Fe oxides, such as goethite (FeOOH). Acid-extractable Ca-P appeared to give a reliable estimate of nonoccluded apatite.

Khin and Leeper (1960) and Fife (1962) found that underestimation of the total amount of P solubilized during NH_4F extraction can be quite pronounced in soils which contain Fe oxides due to P adsorption. Williams et al. (1971) found that Ca fluoride, formed during NH_4F extraction of calcareous materials, sorbed inorganic P, resulting in the formation of a CaF_2-orthophosphate complex. Consequently, the values of NH_4F-P underestimated the amount of inorganic P released from secondary Al- and Fe-containing

sediment components during the NH_4F extractions, whereas the values for "reductant-soluble P" overestimated the amount of P occluded within Fe oxide coating. Williams et al. (1971) proposed a procedure including NH_4Cl, NaOH, DCB, and H_2SO_4 extractions in sequence; while the NH_4F extraction was omitted. The NaOH-extractable P included Al- and Fe-P, and the DCB-P was attributed to resorbed P during the preceding NaOH extraction.

CHAPTER 3
PHOSPHATE MINERALS IN SOME FLORIDA PHOSPHATIC SOILS

3.1. Introduction

Phosphoritic strata outcrop extensively in Florida. Geologists have characterized a number of phosphate minerals in these strata (Altschuler et al., 1956), but the nature and distribution of these minerals in the soil pedon (0 to 2 m) are uncertain. Soil scientists have fractionated P into Al, Fe, Ca, and organic forms using selective-dissolution techniques (Chang and Jackson, 1957; Williams et al., 1967; Steward and Oades, 1972), but have given little attention to direct characterization of specific phosphate minerals. The low level of phosphate minerals in most soils precludes their direct identification (Lindsay and Vlek, 1977). However, Florida soils formed from phosphoritic parent materials (Carlisle et al., 1978, 1981, and 1985) provide an opportunity to study directly the relative stability of phosphate minerals under increasingly intense leaching conditions. The objectives of this study were to determine the phosphate minerals detectable in these soils, and to relate P mineral species to soil properties.

3.2. Materials and Methods

Twelve phosphatic soil pedons from Florida (Table 3.1) with total P exceeding 7 g/kg in B or C horizons were selected for this study. Samples from these pedons were obtained from the University of Florida Soil Characterization Program. They have been described and characterized (Carlisle et al., 1978; Carlisle et al., 1981; Carlisle et al., unpublished). Soils were sampled by horizons to a depth of about 2 m, air-dried, and sieved to remove coarse fragments (>2 mm). For the Mabel soil (Albaquic Hapludalfs), limestone bedrock was encountered at 135 cm.

Samples for mineralogical analysis were dispersed with Na_2CO_3 solution (pH 10) and washed through a 50-μm sieve to separate sand from silt and clay. After drying, the sand was passed through 1-, 0.5-, 0.25-, 0.1-, and 0.056-mm sieves. Material which passed through the 0.056-mm sieve was added to the silt fraction. Silt and clay were separated by centrifugation (Day, 1965). Phosphate minerals in the soil profile were identified by x-ray diffraction (XRD) analysis, using a Nicolet I2 computer-controlled XRD system. Samples were scanned at 2° 2θ per min with CuKα radiation at 35 kV and 20 mA. Oriented mounts of the clay were prepared for XRD by depositing suspended clay onto ceramic tiles under suction, saturating with Mg or K, and washing free of salt. Silt and sand were Na saturated. Silt, sand, and coarse

Table 3.1. Classification and location of pedons studied and total P contents.

Soil classification	County	Total P range†
		g/kg
Soils containing carbonate-fluorapatite [$Ca_{10}(PO_4,CO_3)_6F_{2-3}$]		
Chobee sandy clay loam (fine-loamy, siliceous Typic Argiaquolls)	DeSoto	1.5-30.5
Wabasso sand (sandy, siliceous, hyperthermic Alfic Haplaquods)	DeSoto	0.1-10.5
Mabel fine sand (fine, mixed, hyperthermic Albaquic Hapludalfs)	Levy	0-20.6
Soil containing crandallite [$CaAl_3(PO_4)_2(OH)_5.H_2O$]		
Wauchula fine sand (sandy, siliceous, hyperthermic Ultic Haplaquods)	Polk	0.2-16.5
Soils containing wavellite [$Al_3(PO_4)_2(OH)_3.5H_2O$]		
Blichton fine sand (loamy, siliceous, hyperthermic Arenic Plinthic Paleaquults)	Hernando	0-7.4
Blichton fine sand (loamy, siliceous, hyperthermic Arenic Plinthic Paleaquults)	Levy	1.0-9.0
Bonneau variant fine sand (loamy, siliceous, thermic Arenic Paleudults)	Union	1.5-24.2
Lochloosa variant fine sand (loamy, siliceous, hyperthermic Aquic Arenic Hapludalfs)	Alachua	0.3-20.2
Mulat sand (coase-loamy, siliceous, thermic Typic Ochraquults)	Alachua	0.7-7.6
Norfolk loamy fine sand (fine-loamy, siliceous,thermic Typic Paleudults)	Alachua	1.0-7.9
Ocilla variant loamy fine sand (loamy, siliceous,thermic Aquic Arenic Paleudults)	Union	2.0-42.8
Wacahoota loamy sand (loamy, siliceous, hyperthermic Arenic Ochraquults)	Marion	1.0-20.0

† Total P range is the range in the whole profile.

fragments (> 2 mm) were ground in an agate mortar and packed in a plastic holder for XRD analysis. Quantitative analysis of wavellite in the soils was determined by differential scanning calorimetric analysis (DSC), using the intensity of the endothermic decomposition reaction at 125°C. Since wavellite commonly occurs with quartz and kaolinite in the soils studied, a standard DSC curve for wavellite was plotted as endothermic reaction intensity versus wavellite content in a kaolinite and quartz matrix. For the sand fractions, the ratio of sand with P minerals to sand without P minerals was determined. Cohesion of sand-sized phosphate aggregates (1 to 2 mm in diameter) was determined by ultrasonic dispersion in water adjusted to pH 10. Samples were dispersed in an ultrasonic cleaner for 30 min to record the fraction of > 1-mm sands. Sand counts were made by hand for particles larger than 0.25 mm after mineralogy determination by XRD. Fine sands were counted using a Zeiss polarizing microscope with no. 70c Lakeside brand thermoplastic cement as medium. Total P was determined by Na_2CO_3-fusion (Olsen and Summers, 1982), and Al by KCl extraction (Barnhisel and Bertsch, 1982). Cation exchange capacity (CEC), pH, exchangeable acidity, and base saturation were taken from the soil characterization data base (Carlisle et al., 1978; Carlisle et al., 1981; Carlisle et al., unpublished). The soil pH of each horizon was determined using 1:1 soil/water ratio or soil:1 M KCl

mixtures; extractable bases were determined by summation of the Ca, Mg, Na, and K extracted by 1 M NH_4OAc adjusted to pH 7; extractable acidity was determined by back titration of extracts of $BaCl_2$-TEA using the untreated $BaCl_2$-TEA solution (pH 8.2) as a reference; and CEC was computed as the sum of exchangeable bases and extractable acidity. Base saturation was expressed as the percentage of CEC attributed to bases. Acidic oxalate was used to extract Fe (Sheldrick, 1984).

3.3. Results and Discussion

3.3.1. Phosphate minerals distribution

Carbonate-fluorapatite [$Ca_{10}(PO_4,CO_3)_6F_{2-3}$], crandallite [$CaAl_3(PO_4)_2(OH)_5.H_2O$], and wavellite [$Al_3(PO_4)_2(OH)_3.5H_2O$] were detected in the Florida phosphatic soils (Table 3.1). Variscite ($AlPO_4.2H_2O$) was not found perhaps because it is unstable relative to the other Al hydroxyphosphates (Nriagu, 1976; Flicoteaux and Lucas, 1984). In neutral to acidic environments with low phosphate concentrations, the weathering of calcareous phosphorites may result in the formation of crandallite and wavellite (Nriagu, 1976).

Carbonate-fluorapatite was found in the Btg horizon of Chobee, Wabasso, and Mabel soils, which were located in the land-pebble district of Central and South Florida. Carbonate-fluorapatite was also present in other horizons of Chobee profile except Bt1 horizon. It apparently acted as a cementing material that binds quartz particles in the sand

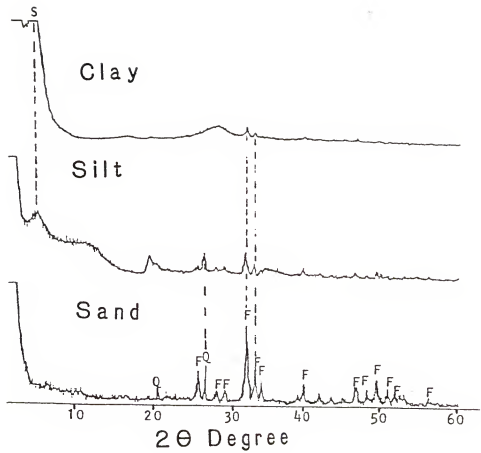

Fig. 3.1. Mineralogy of clay, silt, and carbonate-fluorapatite sand fractions for the Chobee soil (Cg horizon) as shown by XRD. Clay and silt were Mg-glycerol and Na-saturated, respectively. S, F, and Q are smectite, carbonate-fluorapatite, and quartz, respectively.

fraction. A trace of carbonate-fluorapatite also occurred in the silt and clay fractions Fig. 3.1).

The presence of carbonate-fluorapatite in different sand-size fractions of the Chobee soil is shown in Table 3.2. Higher carbonate-fluorapatite counts were found in coarser sands and at greater depth. Total P and clay contents were relatively uniform to a depth of 114 cm. At greater depths, total P increased while clay content decreased (Table 3.3). Rapid increase in total P in the C horizon was due to high carbonate-fluorapatite sand content. Carbonate-fluorapatite sand grains in the Chobee soil are round, suggesting that they have been transported by water. The presence of the Oa horizon indicates a wet soil condition. The Oa horizon had 640 mmol/kg of acetate-extractable Ca, but low KCl-extractable Al (0.1 mmol/kg). Acetate-extractable Ca below the Oa horizon decreased with depth (Table 3.3), because Ca in carbonate-fluorapatite is dominantly in the sand fraction and thus may not be extractable. Base saturation in the Chobee soil was more consistent with depth except for the Oa horizon. Carbonate-fluorapatite sands differed in morphology between horizons of the Chobee soil. The surfaces of carbonate-fluorapatite sand grains in the C horizon (160-198 cm) were brown, smooth and shiny, whereas carbonate-fluorapatite sand grains in the Btg and Oa horizons were gray, and were partly or completely etched, as indicated by surface cavities. The carbonate-

Table 3.2. Counts for quartz (Q) and carbonate-fluorapatite (F) per hundred sand grains in a Chobee soil. The sand fractions contained only quartz and carbonate-fluorapatite particles.

Depth	Horizon	VCS†		CS		MS		FS	
		Q	F	Q	F	Q	F	Q	F
cm		Counts per hundred							
5-0	Oa	95	5	99	1	100	0	100	0
0-13	A	94	6	99	1	100	0	100	0
13-114	Bt1	100	0	100	0	100	0	100	0
114-160	Btg	11	89	69	31	92	8	98	2
160-198	Cg	0	100	32	68	86	14	90	10

† VCS, CS, MS, and FS are 1-2, 0.5-1, 0.25-0.5, and 0.1-0.25 mm sand, respectively;

Table 3.3. Clay content, selected chemical properties and P-mineralogy of Chobee, Mabel, Wabasso, and Wauchula soils.

Depth	Horizon	Clay	O.C.†	Total P	Acet. Ca	KCl Al	CEC	Base sat.	Soil P‡ mineral	pH H_2O
- cm -		- g/kg -		----- mmol/kg ------				%		
					Chobee					
5---0	Oa	298	138	74	640	0.1	94	80	F	5.7
0--13	A	219	31	47	23	0.1	36	71	F	5.6
13-114	Bt1	260	7	55	26	0.5	38	73	No	5.7
114-160	Btg	182	2	325	20	0.3	28	76	F	6.0
160-198	Cg	66	2	986	6	0.0	9	75	F	5.6
					Mabel					
0--18	A	30	11	20	7	0.6	69	24	No	5.0
18--36	E	40	4	26	41	1.1	117	72	No	5.0
36--46	Bt1	380	4	241	37	7.3	242	36	No	4.6
46--79	Bt2	490	2	325	50	9.0	115	44	No	4.5
79-104	Btg1	603	4	439	76	8.2	165	51	No	4.1
104-135	Btg2	798	5	665	156	0.5	488	67	F	4.9
					Wabasso					
0--18	A	13	25	4	6.0	0.5	115	18	No	4.3
18--36	E1	7	5	6	2.7	0.4	35	22	No	4.7
36--53	E2	3	2	2	0.6	0.2	13	20	No	4.9
53--66	E3	5	2	2	0.4	0.2	9	14	No	5.1
66--79	Bh	40	10	21	1.1	5.9	92	6	No	4.7
79--94	Bt1	195	6	96	16.6	16.9	222	23	No	5.0
94-140	Bt2	198	2	66	32.1	11.7	191	44	No	5.2
140-203	Btg	254	1	337	87.5	0.8	30	65	F	5.6
					Wauchula					
0--20	Ap	14	21	2	25.0	3	149	21	No	4.7
20--46	E	7	1	0	1.0	0	44	3	No	5.1
46--74	Bh1	49	10	19	2.0	22	189	2	No	4.5
74-127	Btg1	444	3	221	36.0	26	171	25	C	4.9
127-147	Btg2	511	2	530	61.0	8	188	39	C	5.1
147-173	Cg1	402	1	323	61.0	2	132	59	C	5.1
173-203	Cg2	280	0	314	49.0	0	104	62	C	5.4

† Organic carbon.
‡ F and C are carbonate-fluorapatite and crandallite, respectively; No = None detected.

fluorapatite sands in the Oa, Btg and C horizons all contained carbonate-fluorapatite and quartz, but their resistances to dispersing force were different. After 30 min of dispersion in an ultrasonic bath, all carbonate-fluorapatite sand grains remained intact. However, the supernatant solutions for B-horizon carbonate-fluorapatite were much less clear than for C-horizon material, indicating that carbonate-fluorapatite particles near the surface were more easily disintegrated.

In the Mabel and Wabasso soils, carbonate-fluorapatite occurred only in the Btg2 and Btg horizons, respectively, which had base saturations > 65% (Table 3.3). The pH value was also higher than the overlying horizon in the Wabasso soil, but not in the Mabel soil. However, pH values of soils containing carbonate-fluorapatite are not necessarily higher than those of the soils with crandallite and wavellite (Table 3.3 and 3.4). Carbonate-fluorapatite was not found in the upper horizons of these two pedons, where base saturations were < 50%.

Crandallite was detected only in the silt fraction of the Wauchula soil, in the Btg and C horizons (Fig. 3.2). These horizons had higher acetate-extractable Ca and base saturation than the overlying horizons as well as much higher clay and total P contents (Fig. 3.2). No P mineral was found in those overlying horizons. Minimal eluviation and high Ca activity in the Btg and C horizons may have preserved crandallite in this soil.

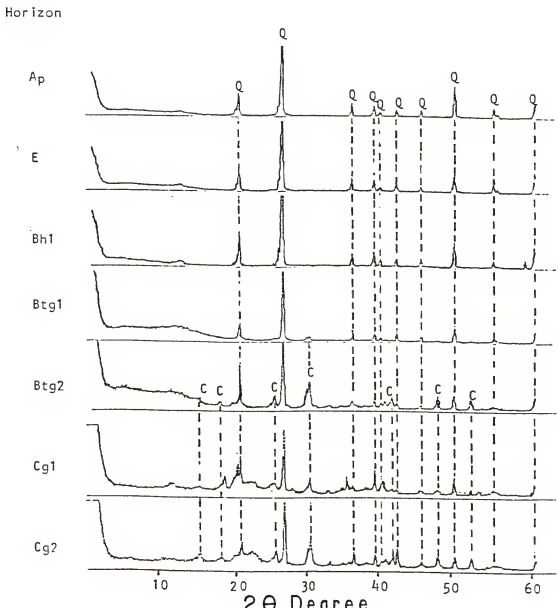

Fig. 3.2. Silt mineralogy for the Wauchula soil as shown by XRD. Silt was Na-saturated. Q and C are quartz and crandallite, respectively.

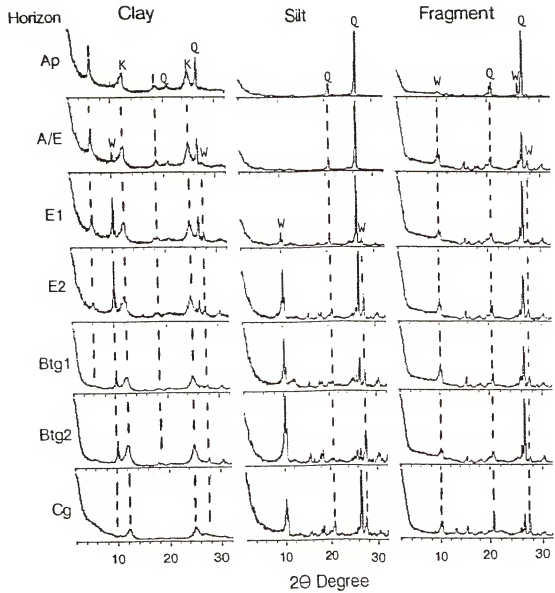

Fig. 3.3. Mineralogy of coarse fragments, silt, and clay fractions of the Ocilla-variant soil as shown by XRD. Clay and silt were K- and Na-saturated, respectively. I, W, K, and Q are hydroxy-interlayered vermiculite, wavellite, kaolinite, and quartz, respectively.

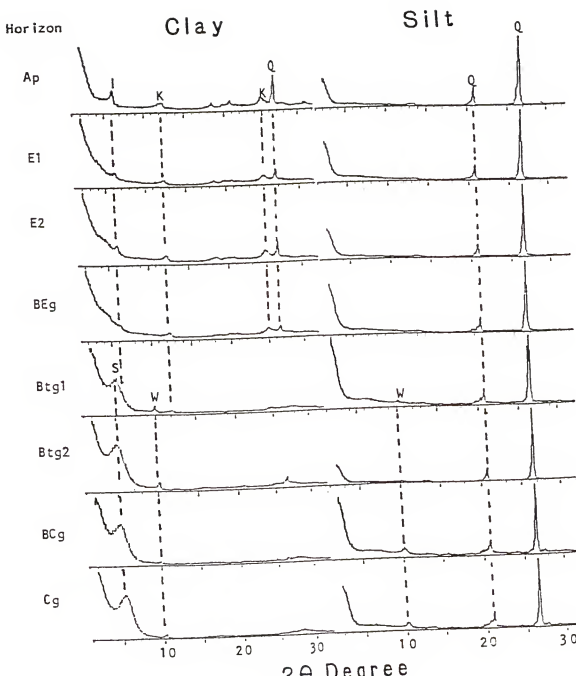

Fig. 3.4. Mineralogy of silt and clay fractions of the Lochloosa-variant soil as shown by XRD. Clay and silt are K- and Na-saturated, respectively. S, I, W, K, and Q are smectite, hydroxy-interlayered vermiculite, wavellite, kaolinite, and quartz, respectively.

Wavellite occurred in all other soils, seven Ultisols and one Alfisol (Table 3.1), indicating its stability under highly weathered conditions. Wavellite was found in Union, Alachua, Levy, and Marion counties in northern Florida, and in Hernando county in central Florida. It is a common component in the upper Al phosphatic zone of the Bone Valley formation of Florida (Altschuler et al., 1956). The occurrence of wavellite in Florida is due to the high parent-rock porosity, which increases the rate of leaching (Flicoteaux and Lucas, 1984). Wavellite was present from the A to the C horizons in Ocilla variant, Lochloosa variant, and Bonneau variant soils. In other soils, wavellite occurred below the A horizon. In the Lochloosa variant, wavellite in the A and E horizons was detected only in the sand or coarse fragments, and not in the silt or clay fraction by XRD (Fig. 3.4, Table 3.5). Since the soils in which wavellite occurred were similar, only the mineralogy of Ocilla variant and Lochloosa variant (Figs. 3.3 and 3.4), and the chemical properties of Wacahoota, Ocilla variant, and Lochloosa variant soils (Table 3.4) are shown. Wavellite was found in clay, silt, and coarse fragments (Fig. 3.3). In the clay fraction, wavellite occurred with smectite (Fig. 3.4), hydroxy-interlayered vermiculite (HIV), and kaolinite (Fig. 3.3). In the silt fraction, it occurred with quartz (Figs. 3.3 and 3.4).

Table 3.4. Clay content, selected chemical properties and P-mineralogy of Wacahoota, Ocilla variant, and Lochloosa variant soils.

Depth	Horizon	Clay	O.C.†	Acet. KCl Ca	Al	CEC	Oxal. Fe	Base sat.	P‡ Mineral	pH H_2O
- cm -		- g/kg -		----- mmol/kg ------				%		
				Wacahoota						
0- 13	Ap	74	17.8	36	0.3	134	20.3	34	No	5.5
13- 74	E	87	5.3	18	1.9	101	26.5	25	W	5.2
74- 96	Btg1	350	5.5	39	16.5	347	64.1	21	W	5.0
96-137	Btg2	324	3.2	23	23.9	318	52.4	19	W	4.6
137-198	BCg	260	2.4	27	19.9	269	60.9	20	W	4.6
				Lochloosa variant						
0- 18	Ap	9	7.1	14.2	0.0	58	10.3	55	No	6.2
18- 53	E1	64	3.0	22.7	0.2	89	26.8	55	No	6.9
53- 79	E2	48	1.2	6.1	2.5	43	24.5	37	No	6.0
79- 89	BEg	157	1.4	20.7	4.6	165	140.0	37	W	5.1
89-137	Btg1	190	0.7	19.8	15.5	220	322.5	25	W	5.0
137-170	Btg2	258	0.3	32.9	21.5	259	104.1	37	W	5.0
170-193	BCg	278	0.5	46.3	21.9	324	249.5	41	W	5.1
193-211	Cg	279	0.2	55.1	19.4	333	149.1	48	W	5.1
				Ocilla variant						
0--15	Ap	68	17	38	0.1	126	44.3	39	W	6.4
13--33	A/E	48	7	10	1.5	71	42.2	19	W	6.2
33--61	E1	50	3	6	2.6	38	27.0	24	W	6.4
61--74	E2	83	2	10	4.3	53	32.8	31	W	6.1
74-127	Btg1	200	2	20	14.3	140	75.6	26	W	5.9
127-175	Btg2	400	1	16	43.4	144	11.1	22	W	5.0
175-203	Cg	497	1	70	57.3	325	35.3	44	W	5.1

† Organic carbon.
‡ W is wavellite; No = None detected.

Coarse fragmental phosphatic materials occurred in most of the soil pedons containing wavellite. In Ocilla variant and Bonneau variant, the fragmental material consisted of wavellite, kaolinite, and quartz (Fig. 3.3). In the groundwater fluctuation zone, most wavellite nodules had a reddish color, probably due to formation of Fe hydroxide coatings with the oxidation of reduced Fe. In Lochloosa variant, all the coarse fragments were reddish-brown in color, indicating the presence of Fe. The soil contained larger amounts of oxalate-extractable Fe compared to that of Ocilla variant (Table 3.4). The presence of Fe hydroxide in the sample reduced XRD peak intensities of other minerals (Fig. 3.4). The presence of wavellite in coarse fragments (>2 mm) and sands was much less common in the A horizon compared to the lower horizons (Table 3.5), reflecting greater weathering in the surface horizon. The coarse fragments in the Ap horizon of Ocilla variant had lower wavellite peak intensities, but higher quartz peak intensities, than those of underlying horizons (Fig. 3.3). Since peak intensity is roughly proportional to mineral content, the lower wavellite peak intensity but higher quartz peak intensity for the coarse-fragments from the Ap horizon suggests that wavellite from this horizon has been lost relative to B and C horizons. Wavellite and kaolinite may have comminuted from coarse fragments into silt and clay fractions, while quartz remained in the sand or silt

Table 3.5. Profile distribution of total P, wavellite sand content, and coarse fragments (Fragments) to fine earth weight-ratio for Wacahoota, Lochloosa variant, and Ocilla variant soils.

Depth	Horizon	Total P	Fragments† Fine earth	Wavellite sand‡ VCS	CS	FS
- cm -		-mmol/kg-	kg/kg	Count per thousand		
			Wacahoota			
0-13	Ap	3	-	0	0	0
13-74	E	87	-	740	40	20
74-96	Btg1	369	-	720	230	140
96-137	Btg2	510	-	580	230	330
137-198	BCg	636	-	180	270	270
			Lochloosa variant			
0-18	Ap	9	0.04	0	10	0
18-53	E1	34	0.33	0	60	10
53-79	E2	26	0.20	0	10	10
79-89	BEg	119	0.76	0	10	70
89-137	Btg1	299	0	210	40	80
137-170	Btg2	462	0	900	300	50
170-193	BCg	492	0	730	230	50
193-211	Cg	651	0	880	370	80
			Ocilla variant			
0-15	Ap	68	0.09	0	0	10
15-33	A/E	66	0.10	110	50	10
33-61	E1	145	1.03	330	130	20
61-74	E2	432	1.30	700	520	90
74-127	Btg1	1145	1.91	850	780	230
127-175	Btg2	1382	1.43	900	520	400
175-203	Cg	654	3.17	910	550	110

† Fragments and fine earth are for soil materials with particle size larger and smaller than 2 mm, respectively.
‡ VCS, CS, and FS are 1-2, 0.5-1, and 0.1-0.25 mm sands, respectively.
- Not determined.

Table 3.6. Profile distribution of wavellite content in clay, silt and wavellite sand (1 to 2 mm), and kaolinite content in clay fraction for Wacahoota, Lochloosa variant, and Ocilla variant soils.

Depth	Horizon	Wavellite content			Clay
		Clay	Silt	sand†	kaolinite
- cm -		--------- g/kg ----------			
		Wacahoota			
0-13	Ap	0	0	0	320
13-74	E	15	15	260	280
74-96	Btg1	15	51	320	310
96-137	Btg2	15	195	250	340
137-198	BCg	262	410	410	350
		Lochloosa variant			
0-18	Ap	0	0	0	240
18-53	E1	0	0	0	190
53-79	E2	0	0	0	240
79-89	BEg	0	0	0	380
89-137	Btg1	45	50	25	340
137-170	Btg2	65	62	23	170
170-193	BCg	50	155	26	190
193-211	Cg	45	185	30	160
		Ocilla variant			
0-15	Ap	22	0	0	330
15-33	A/E	30	40	590	340
33-61	E1	70	105	560	290
61-74	E2	138	190	580	370
74-127	Btg1	104	326	450	450
127-175	Btg2	308	602	580	340
175-203	Cg	52	285	410	490

† Quartz sands cemented by wavellite were included; but pure quartz sands were excluded.

fractions. Therefore, wavellite and kaolinite may have been eluviated while quartz sand remained in the surface. This is suggested because both clay and total P contents increased from the A to Bt2 horizons (Table 3.4 and 3.5) for Ocilla variant, Wacahoota, and Lochloosa variant.

Wavellite has been determined to be more thermodynamically stable than kaolinite (Vieillard et al., 1979), yet wavellite was more depleted in clays and silts of the A horizon than was kaolinite (Fig. 3.3, Table 3.6). Such findings suggest that wavellite may be more unstable compared to kaolinite under soil conditions, possibly as a result of biological processes such as P complexation by root exudates.

3.3.2. Phosphate minerals and soil properties

Species of P minerals are also related to soil chemical properties. Carbonate-fluorapatite, a Ca-P mineral, occurred in soil horizons which had high base saturation, pH, and acetate-extractable Ca; and low KCl-extractable Al. Wavellite, an Al-P mineral, occurred dominantly in the Ultisols, which had higher exchangeable Al and lower base saturation, pH, and acetate-extractable Ca. Crandallite, a Ca- and Al-P mineral, occurred below the Bh horizon in a Spodosol that had intermediate base saturation, acetate-extractable Ca, and KCl-extractable Al (Table 3.7). However, pH values in both water and KCl for soils with crandallite

Table 3.7. Mean and sample standard deviation for selected chemical properties for soils with carbonate-fluorapatite, crandallite, and wavellite in Table 3.1.

P mineral	KCl-Al	Acet.-Ca	Base Sat.	pH		N†
				H_2O	KCl	
	---- mmol/kg -----		%			
Carbonate-fluorapatite	0.3±0.1	156±110	73±2	5.7±0.1	4.8±0.1	12
Crandallite	9.0±5.9	52±6	46±8	5.1±0.1	4.4±0.3	8
Wavellite	11.2±2.6	19±3.3	28±2	5.4±0.1	4.1±0.2	56

† N is the number of horizons of one or more soils which contain the same P minerals.

were not higher than values for soils with wavellite (Table 3.7).

There is a relationship between soil phyllosilicates and dominant P minerals. Smectite, generally associated with less-leached environments (Harris and Carlisle, 1987), was found to occur with carbonate-fluorapatite, crandallite, and wavellite; kaolinite, which may occur in a variety of environments, occurred with crandallite and wavellite, but not with carbonate-fluorapatite. HIV, a mineral associated with near-surface environments, occurred only with wavellite. The sequence of clays and Ca-Al-P minerals in lateritic-weathering profiles of the phosphate plateau of Thies in Senegal was (from least to most stable) carbonate-fluorapatite, calcite, montmorillonite, kaolinite, millisite, crandallite, and wavellite (Vieillard et al., 1979). Smectite and kaolinite may provide Al sources during formation of crandallite and wavellite. However, the formation of crandallite and wavellite in Florida soils is limited by total P content of the soil system. Therefore, these minerals may occur with smectite and kaolinite.

3.4. Summary and Conclusions

Wavellite was the most common phosphate mineral in Ultisols formed from phosphatic materials of northern Florida, indicating the relative stability of wavellite under highly weathered soil conditions. Carbonate-fluorapatite and crandallite were restricted to horizons of

minimal leaching, that had low KCl-extractable Al, and relatively high base status.

Smectite was found in soils with carbonate-fluorapatite and wavellite; kaolinite in soils with crandallite and wavellite; and HIV in soils with wavellite.

Wavellite content in clays and silts increased with depth to a greater extent than did kaolinite content, indicating that wavellite is less stable in highly-leached, near-surface, soil environments.

CHAPTER 4
PRESENCE OF NONCRYSTALLINE
PHOSPHATES IN FLORIDA PHOSPHATIC SOILS

4.1. Introduction

Crystalline phosphate minerals occurring in phosphoritic geologic formations in Florida include carbonate-fluorapatite [$Ca_{10}(PO_4,CO_3)_6F_{2-3}$], millisite [(Na, K)$CaAl_6(PO_4)_4(OH)_9.3H_2O$], crandallite [$CaAl_3(PO_4)_2(OH)_5.H_2O$], and wavellite [$Al_3(PO_4)_2(OH)_3.5H_2O$] (Altschuler et al., 1956). Carbonate-fluorapatite, crandallite, and wavellite also occur in phosphatic soils (Chapter 3). Noncrystalline P materials have not been reported in Florida phosphatic soils. Noncrystalline P would likely be more available to plants due to smaller particle size and high specific surface area. The objectives of this study were (I) to determine the fraction of noncrystalline P; and (II) to relate the noncrystalline P to soil extractable P, Al, Fe, and Ca.

4.2. Materials and Methods

In the previous study (Chapter 3), carbonate-fluorapatite was found present in Chobee sandy clay and Mabel fine sand; Crandallite in Wauchula fine sand; and wavellite in Lochloosa variant fine sand, Ocilla variant fine sand, and Wacahoota loamy sand. Sample from these six

soil profiles and three phosphate minerals were used in the study. Carbonate-fluorapatite from central-Florida phosphoritic geologic deposits, crandallite provided by Minerals Unlimited Company, and a wavellite from Arkansas on sandstone provided by Burnham Petrographic Company were ground to pass 0.1-mm sieve.

Silt and clay were separated by centrifugation (Day, 1965). To confirm the presence of noncrystalline P, carbonate-fluorapatite content in the whole soil, silt, and clay was determined by X-ray diffraction (XRD) according to Klug and Alexander (1974) using a Nicolet I2 computer-controlled XRD system, equipped with graphite crystal monochromator and scintillation detector. Samples were scanned at 2° 2θ per min with CuKα radiation at 35 kV and 20 mA. Corundum (α-Al_2O_3) was used as an internal standard. Samples were ground in an agate mortar and mixed with known weight fraction of corundum before packing in a plastic holder for XRD analysis. Since the CO_3^{-2} content of carbonate-fluorapatite was not known, carbonate-fluorapatite-P was calculated from fluorapatite content assuming the formula $Ca_{10}(PO_4)_6F_2$, with no substitution of Ca^{+2} by other cations or of PO_4^{-3} and F^- by other anions. Actual carbonate-fluorapatite-P could be lower than the calculated one. Quantitative analysis of wavellite in the whole soils and clays was determined by differential scanning calorimetric analysis (DSC), using the intensity of

the endothermic decomposition reaction at 125°C. Since wavellite commonly occurs with quartz and kaolinite in the soils studied (Chapter 3), a standard DSC curve for wavellite was plotted as endothermic reaction intensity versus wavellite content in a kaolinite and quartz matrix. Wavellite P was calculated from wavellite content of the soil.

Total P of the soil, silt and clay, and total soil Ca were determined by the sodium-carbonate fusion method (Olsen and Sommers, 1982). Acidic oxalate (Sheldrick, 1984) was used to extract P, Al, and Fe from the whole soil, silt, and clay. Phosphorus in the oxalate extract was determined by phosphomolybdic blue method (John, 1970) after the residues were ashed at 500°C for 1 hr. Oxalate-extractable Al and Fe were determined by atomic absorption. Dithionite-citrate-bicarbonate (DCB) reagent (Mehra and Jackson, 1960) was used to extract P, Fe, and Al from the soils of the selected horizons. Phosphorus in DCB extraction was determined according to John (1970). After the DCB extraction, the soil residues were washed with 1 N NaCl and extracted with acidic oxalate for P. Selected samples of non-treated soil, oxalate-treated soil, and DCB-treated soil were washed free of salt and were air-dried. The samples again were dried with $CaCl_2$ desiccant overnight and analyzed for heat flow with increasing temperature using DSC.

Phosphate availability indices of the phosphatic soils were determined using Mehlich I (0.05 N HCl + 0.025 N H_2SO_4) (Olsen and Summers, 1982) and Olsen (0.5 M $NaHCO_3$, pH 8.5) extractants (Olsen and Summers, 1982). Triplicate samples were used for all chemical analyses.

4.3. Results and Discussion

4.3.1. Solubility of phosphate minerals

Carbonate-fluorapatite-P, crandallite-P, and wavellite-P were all partially soluble in oxalate and DCB extractants (Table 4.1). The effect decreased in the following order: carbonate-fluorapatite > wavellite > crandallite. The DCB was less effective than oxalate in extracting P from the minerals. The P extractability increased when the minerals to DCB (w/v) ratio was decreased from 0.05 to 0.01.

4.3.2. Presence of noncrystalline Ca-phosphate

Only carbonate-fluorapatite was detected in the clay fraction (C horizon) of Chobee soil and the silt fraction (Bt2 horizon) of Mabel soil. However, carbonate-fluorapatite-P only accounted for a portion of total P. The considerable difference between total P and mineral P indicated the presence of noncrystalline P (Table 4.2). Both oxalate-extractable Al and Fe were lower than oxalate-extractable P in the Chobee clay and the Mabel silt. Phosphate in these samples is associated with mainly Ca, since total Ca is high. The oxalate-P/total P ratio for carbonate-fluorapatite was 0.15; but the ratio for Chobee

Table 4.1. Phosphorus extractability from carbonate-fluorapatite, crandallite, and wavellite by acidic ammonium oxalate and dithionite-citrate-bicarbonate (DCB).

Mineral	Total P	Oxalate-P	DCB-P Mineral-DCB ratio 0.05	DCB-P Mineral-DCB ratio 0.01
	----------	cmol/kg	----------	
Carbonate-fluorapatite	475	69.5±13.7†	2.61±0.03	5.00±0.03
Wavellite	346	24.3± 2.7	2.45±0.03	3.81±0.03
Crandallite	434	12.5± 0.1	1.65±0.06	1.72±0.12

† Each mean and sample standard deviation value was from three replicates.

Table 4.2. Total P and Ca, mineral-P (M-P), oxalate-P (O-P), oxalate-Al (O-Al), oxalate-Fe (O-Fe), and oxalate-P/total P (O-P/Total P) ratio for silt and clay fractions of the phosphatic soils (the lowest horizon in each pedon).

Soil	Horizon	Depth	Total P	Total Ca	M-P†	O-P	O-Al	O-Fe	O-P / Total P
		cm	---------- mmol/kg ----------						
Silt									
Mabel	Btg2	104-135	1061	874	643±59	442	51	208	0.42
Clay									
Chobee	Cg	165-203	926	1243	680±12	836	103	52	0.90
Mabel	Btg2	104-135	658	97	0	164	171	35	0.25
Wacahoota	BCg	137-198	962	58	210±17	211	360	99	0.22
Lochloosa variant	Cg	193-211	703	12	257±19	150	150	221	0.21
Ocilla variant	Cg	175-205	1907	10	189±14	78	171	27	0.04

† Mineral-P in Mabel silt and Chobee clay was in carbonate-fluorapatite form and that in the clays of other soils was in wavellite form.

clay and Mabel silt were 0.9 and 0.42, respectively (Table 4.2). Higher oxalate-extractable P for the Chobee clay and Mabel silt than the carbonate-fluorapatite is probably due to the presence of noncrystalline P. The Mabel clay did not contain carbonate-fluorapatite, but the oxalate-P/total-P ratio was lower than that of the silt. Phosphate in the Mabel clay may be associated with noncrystalline Al or Fe forms since it contained very low total Ca (Table 4.2). The result indicated that carbonate-fluorapatite-P or noncrystalline Ca-P were much more extractable than the noncrystalline Al-P or Fe-P by oxalate due to reaction of oxalic acid with Ca in forming Ca oxalate. The DSC results (Fig. 4.1) showed that for the oxalate-treated soil, there was an endothermic peak at 140°C corresponding to that of Ca oxalate. No Ca oxalate was detected in the Chobee soil before or after DCB treatment.

More P than Al and Fe was extractable by oxalate in Chobee soils (Table 4.3). Although DCB extracted much more Fe than did oxalate from the whole soil fraction of the Mabel Btg2 horizon, the reverse was true for extractable P (Table 4.3) indicating that iron oxide and/or hydroxide was not related with P. Oxalate-P after DCB pretreatment was even higher than that without DCB pretreatment in the Btg2 horizon, suggesting the presence of an oxalate-resistant coating of well crystalline Fe oxide or hydroxide on the Ca-P (Wada, 1977). The Ca-P is more stable under neutral

Table 4.3. Oxalate (Ox)- and dithionite-citrate-bicarbonate (DCB)-extractable P, Al, and Fe; and oxalate-extractable P after DCB pretreatment (Ox-DCB) for selected horizons of soils studied.

Horizon	Depth	P			Al		Fe	
		Ox	Ox-DCB	DCB	Ox	DCB	Ox	DCB
	cm	mmol/kg						
				Chobee				
Bt2g	119-165	82a†	77a	5.5b	43a	1b	6b	12a
Cg	165-203	174a	172a	3.9b	15a	0b	5a	6a
				Mabel				
Bt1	36- 46	59a	15c	46.5b	123a	65b	168b	213a
Btg1	79-104	33a	17c	28.3b	136a	79b	153b	275a
Btg2	104-135	171b	183a	29.5c	196a	75b	33b	193a
				Wacahoota				
Btg1	74- 96	117a	43c	109b	201a	117b	64b	98a
BCg	137-198	115a	92b	115a	122a	86b	61b	118a
				Lochloosa variant				
Btg1	89-137	110b	40c	131a	138a	98b	32b	330a
Btg2	137-170	66b	66b	101a	91a	77b	104b	153a
Cg	193-211	107b	75c	212a	100b	127a	149b	262a
				Ocilla variant				
Btg1	74-127	80a	71b	68.4c	103a	39b	76b	161a
Btg2	127-175	65a	45b	41.0b	111a	50b	12a	10b

† Data of the same element within horizon with the same low case letter were not different at p = 0.05 according to Duncan's test.

conditions than under acidic conditions (Lindsay and Moreno, 1960), and would be less extractable by DCB (a neutral extractant) than by oxalate (an acidic extractant). Therefore, carbonate-fluorapatite and/or noncrystalline Ca-P react with oxalic acid to release P and form a Ca-oxalate precipitate.

4.3.3. Presence of noncrystalline Al- and Fe-phosphates

Although the total P in the clay of the Mabel soil (Btg2) was 658 mmol P/kg, no crystalline P mineral was detected (Table 4.2). The clay fraction of Lochloosa variant, Ocilla variant and Wacahoota soils also contained high total P (703, 1907, and 962 mmol P/kg, respectively), but wavellite P accounted for only 257, 189, and 210 mmol P/kg, respectively. Total Al and Fe were much higher than Ca for these clays (Table 4.2). The noncrystalline P in these clays may be associated with Al and/or Fe.

The DCB extracted more Fe than did oxalate, but the reverse was true for Al (Table 4.3). It has been shown that DCB extracts crystalline and noncrystalline Fe and noncrystalline Al (Wada, 1977), and oxalate extracts noncrystalline Al and Fe (Wada, 1977). Oxalate was also more effective than DCB in extracting P from a reference wavellite mineral (Table 4.1). In the Wacahoota soil, the oxalate-P and DCB-P levels were similar. Both oxalate and DCB extracted considerable amounts of Fe and Al (Table 4.3). Oxalate-P in the soil was associated with both oxalate-Al

and oxalate-Fe (Table 4.6). Oxalate-P in the Ocilla variant soil may be primarily associated with Al, since more P was extractable by oxalate than by DCB; and both oxalate-Al and oxalate-P were higher than oxalate-Fe (Table 4.3). In the Lochloosa variant and Mabel soils (except for the Btg2 horizon of the latter), oxalate-Fe was higher than oxalate-Al, but both were higher than oxalate-P. DCB-P values were higher than oxalate-P. Therefore, P may be associated dominantly with Fe in these soils. Regression analysis indicated that oxalate-P was more closely related with Al than Fe of oxalate extraction in the Ocilla variant soil; but in the Lochloosa variant, Wacahoota, and Mabel soils, the oxalate-P had higher correlation with Fe than with Al of oxalate extraction (Table 4.6).

Results of oxalate-P with and without DCB pretreatment for the whole soils were also compared. For the Chobee and Mabel (Btg2 horizon) soils which contained carbonate-fluorapatite, the oxalate-P before and after DCB pretreatments were not different. For the Lochloosa variant (except Btg2 horizon), Mabel (except Btg2 horizon), and Wacahoota soils, which had high DCB-extractable Fe, oxalate-P was reduced considerably after DCB pretreatment. For the Btg2 horizon of the Ocilla variant soil, with less DCB extractable Fe, DCB pretreatment also reduced the oxalate-P significantly (Table 4.3) indicating that Al-P, probably in noncrystalline form, was also extractable by DCB. DCB was

more effective in removing Fe-P than Al-P. Therefore, for a sample dominated by Al-P, DCB would extract less P, leaving more extractable by oxalate.

The sums of extractable P by oxalate with DCB pretreatment (Ox-DCB) and DCB alone were higher than sums of oxalate (Ox) extraction without DCB pretreatment (Table 4.3). This is because each extraction by either oxalate or DCB would release a certain amount of P until most soil P was removed. Oxalate was not as effective in removing P related to Fe, especially in crystalline forms.

The endothermal DSC peaks from 93 to 97°C may be produced by poorly crystalline Fe and/or Al (Fig. 4.1). The peaks were reduced or absent after oxalate and DCB treatments removed poorly crystalline Al and Fe. Since oxalate and DCB also extract considerable amounts of P (Table 4.3), the poorly crystalline materials may be Fe- and/or Al-P complexes. The difference in extractable Al and Fe by oxalate and DCB also related to the peak intensity in DSC. An endothermal DSC peak occurred at 93° C for the Btg2 horizon of the Ocilla soil (Fig. 4.1). This soil horizon had more extractable Al than Fe and higher oxalate-extractable than those of DCB-extractable Al and Fe (Table 4.3). The DCB treatment reduced the peak intensity only slightly, but the peak disappeared after oxalate treatment. In the Btg1 horizon of the Lochloosa variant soil, which had more DCB-extractable Fe than Al, an endothermal peak occurred at

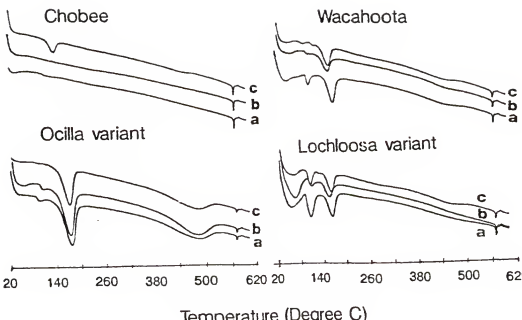

Fig. 4.1. Differential scanning calorimetry (DSC) curves for Chobee (Cg horizon), Ocilla variant (Btg2 horizon), Wacahoota (BCg horizon), and Lochloosa variant (Btg1 horizon) soils. a. No treatment; b. treated with dithionite-citrate-bicarbonate; and c.treated with oxalate.

97°C. The endothermal peak disappeared after the DCB treatment; but the endothermal peak was only reduced slightly by oxalate. For the BCg horizon of the Wacahoota soil, the DCB extracted more Fe than Al, but oxalate extracted more Al than Fe (Table 4.3), both oxalate and DCB reduced the intensity of an endothermic peak at 96°C. Therefore, the endothermal peak for the Ocilla variant soil may be produced dominantly by noncrystalline Al, while that for Lochloosa variant soil may be produced dominantly by noncrystalline Fe. In Wacahoota soil, both noncrystalline Fe and Al contributed to the endothermal peak.

4.3.4. Distribution of oxalate-extractable P in soil profiles

Total P and oxalate-P increased with depth in the Chobee and Mabel soils. But the oxalate-P/total P ratio in the profile varied with soil. In the Chobee soil, the ratio was slightly lower for O and C horizons than for A and B horizons (Table 4.4). No P mineral was detected from the A to Bt1 horizons which had comparable amounts of total P to that of the O horizon. Carbonate-fluorapatite was detected in the sand and silt fractions of both Bt2 and C horizons. Clay from Cg horizon contained 926 mmol/kg P, which was only partly in mineral form (Table 4.2).

In the Mabel soil, carbonate-fluorapatite occurred only in the Btg2 horizon. Both oxalate-P and total P increased with depth, but the oxalate-P/total P ratio decreased with

Table 4.4. Total Ca and P; mineral-P (M-P); ratio of mineral-P to total P (M-P/T-P); oxalate-extractable P, Al, and Fe; oxalate-P to total P ratio (O-P/T-P); and the ratio of oxalate-P to the sum of Al and Fe of oxalate extracts (O-P/Al+Fe) by horizon for phosphatic soils.

Horizon	Depth	Total		M-P†	M-P / T-P	Oxalate			O-P / T-P	O-P / Al+Fe
		Ca	P			P	Al	Fe		
	cm	-- mmol/kg --				--- mmol/kg ---				
Chobee										
Oa	5---0	76	74	6	0.08	14.5	49.6	7.5	0.20	0.25
A	0--13	24	47	2	0.04	10.8	28.0	6.1	0.23	0.32
Bt1	13--63	20	51	0	0	10.9	15.5	6.4	0.21	0.50
Bt1	63-114	27	59	0	0	13.9	39.0	5.1	0.24	0.32
Bt2g	114-160	281	325	213	0.65	81.6	39.2	5.9	0.25	1.81
Cg	160-198	1941	986	813	0.82	173.9	14.7	5.2	0.18	8.74
Mabel										
A	0--18	9	20	0	0	7.5	23.2	33.8	0.38	0.13
E	18--36	10	26	0	0	9.1	23.1	33.0	0.37	0.16
Bt1	36--46	17	241	0	0	58.7	122.7	140.4	0.22	0.22
Bt2	36--79	18	325	0	0	66.1	114.0	165.6	0.24	0.24
Btg1	79-104	30	439	0	0	32.5	136.5	150.6	0.09	0.11
Btg2	104-135	270	665	223	0.33	170.7	196.3	32.8	0.28	0.75
Wauchula										
Ap	0--20	3	6	-‡	-	0.4	10.6	28.2	0.07	0.01
E	20--46	2	5	-	-	0.2	0.4	20.3	0.04	0.00
Bh1	46--61	2	22	-	-	3.6	51.3	18.7	0.16	0.04
Bh2	61--74	15	26	-	-	7.7	73.2	16.6	0.29	0.07
Btg1	74-127	115	221	-	-	4.3	56.6	57.6	0.02	0.04
Btg2	127-147	141	530	-	-	12.2	51.9	51.9	0.02	0.12
Cg1	147-173	124	323	-	-	5.4	33.9	13.3	0.02	0.11
Cg2	173-203	169	314	-	-	7.1	25.2	12.8	0.03	0.19

Table 4.4. (Continued).

Horizon	Depth	Total Ca	Total P	M-P†	M-P / T-P	Oxalate P	Oxalate Al	Oxalate Fe	O-P / T-P	O-P / Al+Fe
	cm	-- mmol/kg --				---- mmol/kg ----				
					Wacahoota					
Ap	0-13	44	3	0	0	1.0	5.7	20.0	0.35	0.04
E	13-74	26	87	12	0.14	27.0	47.0	26.4	0.30	0.37
Btg1	74-96	54	369	79	0.21	117.0	200.8	64.0	0.31	0.44
Btg2	96-137	53	510	168	0.33	56.4	152.2	52.4	0.11	0.28
BCg	137-198	51	636	368	0.58	114.7	122.2	60.9	0.18	0.63
					Lochloosa variant					
Ap	0-18	57	9	0	0	2.9	12.3	21.4	0.33	0.09
E1	18-53	61	34	2	0.06	17.9	73.3	55.5	0.52	0.14
E2	53-79	14	26	1	0.04	10.9	47.8	47.3	0.42	0.11
BEg	79-89	45	119	19	0.16	70.7	108.3	290.6	0.59	0.18
Btg1	89-137	54	299	112	0.49	109.7	138.0	667.5	0.36	0.14
Btg2	137-170	76	462	292	0.63	66.5	90.8	215.3	0.14	0.22
BCg	170-193	79	492	244	0.50	105.8	101.8	516.7	0.21	0.17
Cg	193-211	92	651	330	0.51	107.1	100.0	308.7	0.16	0.26
					Ocilla variant					
Ap	0-15	55	68	12	0.18	28.7	47.8	44.3	0.42	0.31
A/E	15-33	25	66	15	0.22	25.9	48.9	42.2	0.39	0.28
E1	33-61	17	145	102	0.70	22.0	42.4	27.0	0.15	0.31
E2	61-74	26	432	337	0.78	45.1	76.1	32.8	0.10	0.41
Btg1	74-127	48	1145	1094	0.96	80.3	102.7	75.6	0.07	0.45
Btg2	127-175	65	1382	1094	0.79	65.0	111.6	11.1	0.04	0.53
Cg	175-203	103	654	556	0.85	73.2	100.0	35.3	0.11	0.54

† Mineral P of Chobee and Wabasso soils were in fluorapatite form; and that of Wacahoota, Lochloosa variant, and Ocilla variant soils were in wavellite form.

ǂ - Not determined.

depth indicating the increase in P crystallinity with depth (Table 4.4).

In the Wauchula soil, which contained crandallite, the oxalate-P increased with total P. The oxalate-P/total P ratios were from 0.02 to 0.03 for all the (Bt and Cg) horizons with crandallite indicating the low extractability of crandallite P by oxalate.

The Lochloosa variant, Ocilla variant, and Wacahoota soils contained wavellite as determined by XRD and DSC; but wavellite-P was only a fraction of total P in the whole profile of the phosphatic soils (Table 4.4). The wavellite-P to total-P ratio increased from A to B horizons. Total P also increased from A to B horizons. Generally, the oxalate-P/total-P ratio increased with the decrease in oxalate-P/(oxalate-Al + Fe) ratio (Table 4.4). The oxalate-P/total P ratio for pure wavellite was only 0.07, but the ratio for soils were much higher except for the B horizons of the Ocilla variant soil. Total P, wavellite-P, and wavellite-P/total P ratio increased from the surface to the Bt horizon (Table 4.4). The results indicated that crystalline P minerals are relatively unstable in eluvial horizons. Lochloosa variant and Wacahoota soils had higher noncrystalline-P to total-P ratios than the Ocilla variant soil. Lochloosa variant and Wacahoota soils contained abundant Fe mottles and noncrystalline nodules. The

noncrystalline Fe hydroxide may retain P and give a lower wavellite-P to total-P ratio.

4.3.5. Phosphorus availability indices

The soil extractable P by Mehlich I and Olsen extractants reflect phosphate availability (Olsen and Summers, 1982). Only a small portion of the soil total P from the phosphatic soils was extractable by Olsen and Mehlich I extractants (Table 4.4 and 4.5). Soils varied in their release of P using these extractants. Olsen-P was less than Mehlich I-P in the Chobee soil which contained carbonate-fluorapatite or noncrystalline Ca-P (Table 4.5). The amounts of Olsen-P in the profile ranged from 0.5 to 1.5 mmoles/kg despite the large amount of total P in the Btg2 and C horizons (Table 4.4). Mehlich I-P increased from 1.5 mmol/kg at the Oa horizon to 81 mmol/kg at the C horizon due to the increase in carbonate-fluorapatite content at Btg2 and C horizons. The Mehlich I-P has been shown to be highly correlated with Ca-P (Sartain, 1978; Chang and Juo, 1963). Carbonate-fluorapatite was more soluble in the Mehlich I reagent due to high acidity (Lindsay and Moreno, 1960). The Mehlich I-Ca, probably a product of carbonate-fluorapatite dissolution, also increased from the E horizon to the C horizon (Table 4.5). However, the correlation between Ca and P in Mehlich I extracts from various horizons of Chobee soil was lower than that between Al or Fe and P (Table 4.6). This was because the Mehlich I-P was low but the Mehlich I-Ca was

Table 4.5. Olsen- and Mehlich I-extractable P, Fe, Al, and Ca distribution in the soil profile for the phosphatic soils.

Horizon	Depth	Olsen	Mehlich I			
		P	P	Fe	Al	Ca
	cm	mmol/kg				
			Chobee			
Oa	5---0	0.82±0.02†	1.52±0.04	0.07	2.32	67.72
A	0--13	0.39±0.01	2.02±0.08	0.19	0.03	26.93
Bt1	13--63	0.73±0.03	2.36±0.24	0.24	0.02	19.96
Bt1	63-114	0.71±0.02	5.31±0.52	0.22	3.97	22.57
Bt2g	114-160	1.25±0.06	64.68±0.73	1.35	10.74	51.10
Cg	160-198	0.61±0.08	80.90±0.11	1.96	4.71	57.85
			Wauchula			
Ap	0--20	0.15±0.01	0.16±0.01	1.45	3.98	3.86
E	20--46	0.03±0	0.02±0	0.14	0.10	0.01
Bh1	46--61	1.84±0.08	0.46±0.01	0.51	0.36	0.37
Bh2	61--74	3.53±0.07	1.50±0.08	0.14	0.16	0.17
Btg1	74-127	0.29±0.05	0.13±0	0.32	2.65	2.66
Btg2	127-147	0.27±0.01	0.42±0.01	0.13	6.00	5.99
Cg1	147-173	0.41±0.01	0.42±0.01	0.11	3.92	3.92
Cg2	173-203	0.60±0.02	0.54±0.02	0.11	2.82	2.82
			Wacahoota			
Ap	0-13	0	0.02±0	0.05	0.68	0.04
E	13-74	2.34±0.15	4.45±0.16	0.77	12.38	3.72
Btg1	74-96	10.98±0.13	14.81±0.07	0.92	41.55	9.95
Btg2	96-137	9.47±0.09	12.30±0.30	1.29	28.33	5.02
BCg	137-198	6.63±0.37	11.15±0.06	1.89	16.70	8.57

Table 4.5. (Continued).

Horizon	Depth	Olsen P	Mehlich I P	Mehlich I Fe	Mehlich I Al	Mehlich I Ca
	cm	mmol/kg				
			Lochloosa variant			
Ap	0-18	0.10±0.01	0.16 0.33	0.16	2.11	5.71
E1	18-53	0.99±0.02	2.30±0.03	0.52	6.77	6.97
E2	53-79	0.73±0.02	1.15±0.03	0.33	5.92	2.13
BEg	79-89	3.98±0.11	3.59±0.23	1.85	13.62	8.84
Btg1	89-137	4.63±0.01	4.89±0.07	2.25	13.17	7.80
Btg2	137-170	1.82±0.03	2.66±0.02	0.93	3.75	7.19
BCg	170-193	2.33±0.06	2.58±0.03	0.80	3.21	9.83
Cg	193-211	2.33±0.08	2.95±0.05	0.46	2.63	12.74
			Ocilla variant			
Ap	0-15	1.93±0.04	3.89±0.04	0.60	14.91	3.89
A/E	15-33	2.20±0.13	3.75±0.06	0.69	9.61	3.75
E1	33-61	1.54±0.01	2.59±0.05	0.56	8.33	1.06
E2	61-74	2.07±0.06	2.32±0.03	1.33	4.73	1.76
Btg1	74-127	4.22±0.09	2.65±0.07	3.62	4.54	3.85
Btg2	127-175	1.50±0.03	1.79±0.03	0.27	4.24	2.23
Cg	175-203	2.49±0.02	3.23±0.05	0.49	5.22	8.12

† The mean and sample standard deviation was from three replicates.

high in Oa horizon, which contained high organic carbon but low total P. The high Ca was probably from the organo-Ca complex. The Olsen-P was correlated with Mehlich I-Al (Table 4.6). The total P was much lower in the Bh horizons of the Wauchula soil than the Bt and C horizons in which crandallite occurred. However, the Olsen-P and Mehlich I-P of the Bh horizons were much higher than those of the underlying horizons (Table 4.5). The Mehlich I-Al content in the Bh horizons was also higher than that of the other horizons. Both Mehlich I-P and Olsen-P were correlated with Mehlich I-Al (Table 4.6). The Olsen-P of Bh horizons was higher than the Mehlich I-P. The 0.5 M $NaHCO_3$ extractant was used to extract the labile pool of organic P (Bowman and Cole, 1978). Crandallite occurred from the Bt to C horizon of the Wauchula soil. These horizons contained high total P, ranging from 221 to 530 mmoles/kg, but they yielded less than 1 mmol/kg P by either Mehlich I or Olsen extractants.

Wavellite occurred in the Ocilla variant, Lochloosa variant, and Wacahoota soils. The Ap and A/E horizons of Ocilla variant contained more Mehlich I-P than the B horizons although total P content was lower than that of the B or C horizons (Table 4.5). In the Lochloosa variant and Wacahoota soils, both Mehlich I-P and Olsen P of the Ap horizon were less than 0.2 mmol/kg due to low total P (9 and 3 mmol/kg, respectively). The highest Mehlich I-P and Olsen P occurred in the Btg1 horizon of the Lochloosa variant and

Wacahoota soils (Table 4.5). The highest Olsen P of the Ocilla variant soil was also found in the Btg1 horizon which contained high Mehlich I-Fe (Table 4.5). However, the total P in the Btg1 horizon for all the three soils was lower than that of the Btg2 and BC horizons. The higher Olsen-P and Mehlich-I P in the Bt1 horizon than the Btg2 and BC horizons may be due to higher noncrystalline P, especially that associated with Fe. Both Mehlich I-P and Olsen P were significantly correlated with Fe, Al, and Ca of Mehlich I extraction in the Lochloosa variant and Wacahoota soils. The Mehlich I-P was correlated with Mehlich I-Al and Ca, but the Olsen P was correlated with Mehlich I-Fe in the Ocilla variant soil. Apparently, noncrystalline P was associated with Al and Ca in the Ap and E horizons, but with Fe in the Btg1 horizons (Table 4.5).

In the three soils containing wavellite, Olsen P was commonly lower than Mehlich I-P. Exceptions were the BEg and Btg1 horizons of the Lochloosa variant and the Btg1 horizon of the Ocilla variant soils which had higher extractable Fe than the other horizons.

Mehlich I-P and Olsen P were not proportional to the total P content in the Ocilla variant, Lochloosa variant, and Wacahoota soils containing wavellite. In the Ocilla variant soil, maximum total P occurred at the Btg2 horizon, but Mehlich I-P in this horizon was the lowest. Of the three soils, the Wacahoota soil has the highest Mehlich I-P and

Table 4.6. Pearson correlations of Mehlich I-P, Olsen-P, and Oxalate-P with Fe, Al, and Ca by Mehlich I extraction and Al and Fe by oxalate extraction for all horizons of the phosphatic soils.

	Mehlich I-extractable			Oxalate-extractable	
	Fe	Al	Ca	Al	Fe
			Chobee		
Mehlich I-P	0.99***†	0.73**	0.50*	-0.29	-0.36
Olsen P	0.35	0.78***	0.42	0.48*	0.13
Oxalate-P	0.97***	0.51*	0.52*	-0.42	-0.35
			Mabel		
Oxalate-P				0.81**	0.92***
			Wauchula		
Mehlich I-P	-0.30	0.85***	-0.29	0.67**	-0.34
Olsen P	-0.18	0.96***	-0.56**	0.68**	-0.36
Oxalate-P	-0.54*	0.20	0.45*	0.65**	0.26
			Wacahoota		
Mehlich I-P	0.72**	0.92***	0.90***	0.98***	0.96***
Olsen P	0.61*	0.95***	0.83***	0.99***	0.92***
Oxalate P	0.76**	0.74**	0.97***	0.85***	0.95***
			Lochloosa variant		
Mehlich I-P	0.88***	0.59*	0.52*	0.96***	0.82***
Olsen P	0.94***	0.55*	0.48*	0.91***	0.84***
Oxalate-P	0.58*	0.03	0.78***	0.67**	0.90***
			Ocilla variant		
Mehlich I-P	-0.13	0.84***	0.61*	-0.57	0.39
Olsen P	0.92***	-0.25	0.15	0.40	0.97***
Oxalate-P	0.50*	-0.76***	0.17	0.94***	0.27

† *, **, and *** = Pearson correlation coefficient significant at 0.05, 0.001, and 0.0001 levels, respectively.

Table 4.7. Linear regression relation between Mehlich I-extractable P or Olsen-extractable P (mmol/kg) and oxalate-extractable P (OP) (mmol/kg) for the phosphatic soils.

Regression equations						r†	pr>F
Chobee							
Mehlich I-P	=	(-0.568)	+	0.522*OP		0.95	0.0001
Olsen-P	=	0.737	+	0*OP		0.10	0.69
Wacahoota							
Mehlich I-P	=	1.97	+	0.104*OP		0.89	0.0001
Olsen-P	=	0	+	0.072*OP		0.81	0.0003
Lochloosa variant							
Mehlich I-P	=	0.974	+	0.025*OP		0.80	0.0001
Olsen-P	=	0.429	+	0.027*OP		0.79	0.0001
Ocilla variant							
Mehlich I-P	=	3.54	-	0.013*OP		0.42	0.058
Olsen-P	=	1.12	+	0.024*OP		0.62	0.003

† r is the correlation coefficient of the regression.

Olsen P. The differences in extractable P in these phosphatic soils were obviously due to presence of different amounts of noncrystalline P.

The Mehlich I extractant dissolved much more P than did Olsen extractant in the Chobee soil (Table 4.5). The Mehlich I-P was a linear function of Oxalate-P for the Chobee soil, while the Olsen P was not (Table 4.7). For the Lochloosa variant, Ocilla variant, and Wacahoota soils, both Mehlich I-P and Olsen P were significantly related to oxalate-P, and therefore to noncrystalline P content.

4.4. Summary and Conclusions

The presence of noncrystalline phosphates in the phosphatic soils was inferred by low wavellite-P/total P or carbonate-fluorapatite-P/total P ratios but high oxalate-P/total P ratios. The Ca-P was extractable by oxalate but not by DCB. Both oxalate and DCB extracted noncrystalline Fe- or Al-P, but DCB is more effective in removing P associated with Fe. Both Olsen-P and Mehlich I-P varied among the phosphatic soils even with soils containing the same phosphate mineral. The Olsen-P and Mehlich I-P were linear functions of oxalate-P from the soils containing wavellite. Both Mehlich I- and Olsen-extractable P were higher in Btg1 or B/E horizon compared to that of the underlying horizons. The high extractable P in the B/E or Btg1 horizon was due to higher poorly crystalline Fe- and Al-P materials.

CHAPTER 5
RELATION BETWEEN PHOSPHORUS AND IRON IN FLORIDA PHOSPHATIC SOILS

5.1. Introduction

Iron-P minerals are uncommon in the Florida phosphatic soils (Chapter 3). Flicoteaux and Lucas (1984) concluded that meteoric waters lead to the generation of Fe-phosphates only in the absence of clayey material, or in very reducing conditions. Phosphate ion reactions with Fe-hydroxides occur much more slowly than with Al-hydroxides (Haseman et al., 1951; Kittrick and Jackson, 1955; Taylor et al., 1964; Taylor and Gurney, 1965). However, Al-phosphates may, with age, transform to Fe-phosphate (Yuan et al., 1960; Shelton and Coleman, 1968; Chang and Chu, 1961). Phosphate can inhibit crystalline Fe mineral formation (Schwertmann and Taylor, 1977). Golden and Dixon (1985) found that the presence of phosphate as an adsorbed anion on kaolinite did not inhibit Fe-oxide crystallization from ferric hydroxide gel. The strong interaction between P and kaolinite leaves little P in the solution to interact with ferric hydroxide. Iron nodules occur in some Florida phosphatic soils (Carlisle et al., 1981). The effect of P on the formation of crystalline Fe-oxide or hydroxide in these nodules and within the soil materials is not well known. The objectives

of this research were (i) to study the relationships between P and Fe in Florida phosphatic soils, and (ii) to determine the effect of P on crystalline Fe mineral formation in controlled laboratory incubation studies.

5.2. Materials and Methods

5.2.1. Materials

Soils and Fe nodules (1 to 2 mm) from selected subsurface horizons of five phosphatic soils were used. Wabasso fine sand contained carbonate-fluorapatite. The other four soils; Bonneau variant fine sand, Lochloosa variant fine sand, Norfolk loamy fine sand, and Blichton fine sand contained wavellite (Table 3.1). Four non-phosphatic soils rich in Fe were also selected from Florida, including Lochloosa fine sand (loamy, siliceous, hyperthermic Arenic Paleudults) from Hernando county, Fuquay loamy sand (loamy, siliceous, thermic Arenic Paleudults) from Walton county, Pineda loamy very fine sand (siliceous, hyperthermic Arenic Glossaqualfs) from Pasco county, and Vero sand (sandy-over-loamy, siliceous, hyperthermic Alfic Haplaquods) from Lee county.

5.2.2. Soil study

Soil materials were analyzed to relate the crystallinity and extractability of Fe to P extractability. Both soils and Fe nodules were ground to pass 100-mesh sieve and analyzed for total P by the Na_2CO_3 fusion method (Olsen and Summers, 1982). Total Fe, Al, and Ca from Fe nodules

were also determined by Na_2CO_3 fusion. Oxalate-extractable P, Si, Al, and Fe (Sheldrick, 1984); and Mehlich I- (0.05 N HCl + 0.025 N H_2SO_4) and Olsen-extractable P (0.5 N $NaHCO_3$, pH 8.5) (Olsen and Summers, 1982) were determined for the soils. An Ocilla variant soil (loamy, siliceous, thermic Aquic Arenic Paleudults), which contained wavellite but did not contain Fe nodules, was also analyzed for Mehlich I- and Olsen-P. The dithionite-citrate-bicarbonate (DCB)-extractable Fe, Al, and P were determined using a 1-g sample in a 100-ml centrifuge tube. A 40-ml aliquot of 0.3 M sodium citrate, 5-ml of 1 M $NaHCO_3$, and 1-g of $Na_2S_2O_4$ were added. The samples were heated in the water bath to 80°C for 20 min and centrifuged to obtain the clear supernatant solution. The DCB treatment was repeated until all the samples changed to a gray color. The total Ca, Fe, and Al and the oxalate- and DCB-extractable Fe and Al were determined by atomic absorption analyses. The DCB- and oxalate-extractable P were determined by phosphomolybdic blue method (John, 1970). The oxalate-extractable Si (Sheldrick, 1984) was determined by blue silicomolybdous acid procedure (Kilmer, 1965).

Mineralogy of clays and nodules was determined by X-ray diffraction analysis (XRD), scanning at 2° 2θ per min using CuKα as the source radiation. Oriented mounts of the clay were prepared for XRD by depositing the clay suspensions onto ceramic tiles under suction, saturating with Mg, and washing free of salt. The Fe nodules were crushed using an

agate mortar, and packed in a plastic holder for XRD analysis. Samples of crushed Fe nodules were extracted with DCB and then fractionated into sand, silt, and clay. The sand (< 0.1 mm)-, silt-, and clay-size fractions of the nodules were also analyzed for mineralogy by XRD. The crused Fe-nodules was also analyzed by differential scanning calorimetry (DSC) from room temperature to 600°C. Grain counts of the Fe-nodules with depth were made using a petrographic microscope.

Cation exchange capacity (CEC), pH, base saturation, and particle size distribution data were taken from the soil characterization data base. Extractable bases (Ca, Mg, Na, and K) were replaced by leaching 10 g of soil 5 times with 20 ml of 1 M NH_4OAc bufferd at pH 7.0. Calcium and Mg were determined by atomic absorption, and K and Na by flame emission. Extractable acidity was measured by using $BaCl_2$-triethanolamine (pH 8.2). The CEC was calculated from the sum of extractable cations and acidity. Base saturation was obtained from the ratio of extractable bases to the sum of extractable cations and acidity. Particle size distribution was determined by a modified pipette method (Carlisle, et al., 1978; Carlisle, et al., 1981; Carlisle, et al., 1985; Carlisle, et al., unpublished).

5.2.3. Synthesis of iron minerals

A laboratory study was also conducted to determine the restricting effect of P on Fe crystallization. Ferric

hydroxide [$Fe(OH)_3$] suspension was prepared from 25.0 ml of 0.2 M ferric nitrate [$Fe(NO_3)_3.9H_2O$] neutralized with 1 M NaOH to pH 5.0. The suspension was centrifuged to remove salt. The precipitate was washed once with 30-ml water and centrifuged. The ferric hydroxide precipitate was washed into a 125-ml Erlenmeyer flasks with 50 ml water. An aliquot of 0 or 5.0 ml of 0.1 M KH_2PO_4 was mixed with ferric hydroxide suspension. The suspension was brought to a 120-ml volume with deionized H_2O and pH was adjusted to 5.0. Another preparation was made but was adjusted to pH 12.0. A 25.0-ml portion of 0.2 M ferric nitrate solution was also directly mixed with 0 or 5.0 ml of 0.1 M KH_2PO_4. The suspension was adjusted to pH 5.0 with 1 M NaOH without removing salt and was brought to 120 ml volume with deionized H_2O.

In the phosphatic soils, P, Si, Al, and clay minerals were all present. To compare the effects of P with those of Si and the common clay minerals on Fe crystallization, 0.5 mmoles of silicic acid powder [$Si(OH)_4$] or 0.15 g of kaolinite, montmorillonite, vermiculite, or gibbsite was also mixed with ferric hydroxide suspension which had been washed free of salt. To determine the effect of Al, 5 ml of 0.1 M Al nitrate [$Al(ON_3)_3.9H_2O$] was mixed with 25 ml of 0.2 M Fe nitrate, neutralized with 1 M NaOH to pH 5.0, centrifuged and washed once with 30 ml water to remove salt.

All the suspensions were brought to 120 ml volume by water, and adjusted to pH 5.0 and 12.0, respectively.

Since reaction rate increases with temperature, all the treatments were incubated in an oven at 80±2°C. Each flask was covered with a rubber stopper when the solution temperature was raised to about 80°C and incubated for 3 wks. Water loss was negligible during incubation. At the end of incubation, a portion of each precipitate was taken to determine oxalate-extractable Fe. The mineralogy of the precipitates was determined by XRD.

Weight loss of the precipitated samples were determined by thermogravimetric analysis (TGA) from 25 to 600°C after they were air-dried and subjected to desiccation in $CaSO_4$ at room temperature. Water content of the precipitates was calculated from percentage of weight loss determined by TGA assuming all weight loss was due to water loss and all structural water of the samples were lost at 600°C.

5.3. Results and Discussion

5.3.1. Nature of iron nodules

No goethite or hematite was detected in the Fe nodules of the phosphatic soils by XRD (Fig. 5.1a) although the DCB-extractable Fe (DCB-Fe) was higher than 260 cmol/kg (Table 5.1). The Fe nodules of Lochloosa variant, Norfolk, and Blichton soils showed a broad peak ranging from 21 to 23° 2θ (d = 4.23-3.86 Å). This peak probably arose from the poorly crystalline Fe oxides or hydroxides (Fig. 5.1a), since it

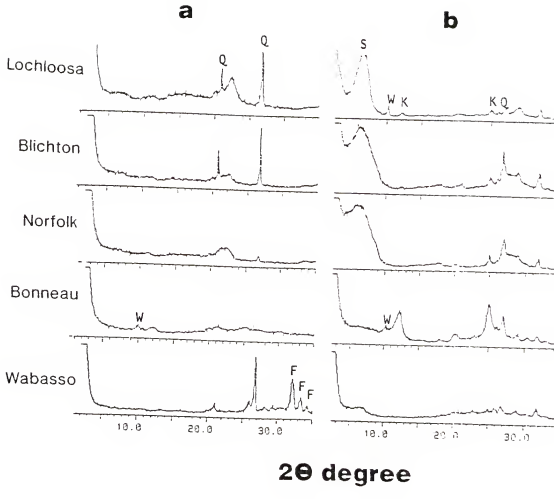

Fig. 5.1. Results of x-ray diffraction analysis of Fe nodules. (a) The whole Fe nodules and (b) the clay-size fraction of the Fe nodules after dithionite-citrate-bicarbonate pretreatment. The fine-sand-size and silt-size fractions of the Fe nodules not shown are quartz and wavellite or carbonate-fluorapatite. F = carbonate-fluorapatite, K = kaolinite, Q = quartz, S = smectite, W = wavellite.

disappeared after DCB pretreatment (Fig. 5.1b). The Fe nodules of the Wabasso and Bonneau variant did not show this broad XRD peak. The total Fe of the Fe nodules determined by the Na_2CO_3 method (Olsen and Summers, 1982) were lower than DCB-extractable Fe (Table 5.1). The reason was that Fe in the nodules was not completely soluble by H_2SO_4 after fusion with Na_2CO_3.

The P content of the nodules ranged from 55 to 183 cmol/kg. The Fe nodules of the Wabasso soil had the highest total P content because of the presence of carbonate-fluorapatite as indicated by XRD (Fig. 5.1a) and by high total Ca content (Table 5.1). Wavellite was detected in the Bonneau variant and Lochloosa variant soils before and after the DCB treatment (Fig. 5.1).

In addition to high DCB-extractable Fe, a range of 21.6 to 44.4 cmol/kg P was extracted by DCB from the Fe nodules (Table 5.1), indicating a relation between Fe and P. The ratio of DCB-P to DCB-Fe in the Fe nodules ranged from 0.07 in the Norfolk soil to 0.12 in the Lochloosa variant soil. The DCB-P may be dominantly noncrystalline or poorly crystalline Fe-P and reductant soluble P (Chang and Jackson, 1957). The DCB-P in the Fe nodules of Norfolk and Blichton soils was higher than that of the Wabasso, Lochloosa variant, and Bonneau variant soils (Table 5.1) which contained carbonate-fluorapatite or wavellite. Carbonate-fluorapatite and wavellite largely remained after the DCB

Table. 5.1. Total P, Fe, Al, and Ca by Na_2CO_3 fusion and dithionite-citrate-bicarbonate (DCB)-extractable Fe, Al, and P of 1-2 mm-size Fe nodules from the phosphatic soils.

Soil	Horizon	Total				DCB		
		Fe	Al	Ca	P	Fe	Al	P
		cmol/kg						
Blichton	BCtg	274	90	1	55	462	29.1	38.0
Bonneau variant	B/E	332	167	1	76	284	41.4	21.6
Lochloosa variant	Btg1	164	80	1	65	267	28.2	34.4
Norfolk	C	383	128	1	56	618	39.4	44.3
Wabasso	Btg3	195	60	251	183	364	28.0	28.2

treatment indicating that DCB extracts only a small amount of P from these minerals. However, carbonate-fluorapatite was not detected in the clay-size fraction of Fe nodules of the Wabasso soil after DCB treatment (Fig. 5.1b) because it occurred in the the fine sand fraction of the nodules (not shown). Aluminum was also extracted by DCB (Table 5.1) indicating that some poorly crystalline Al forms (Wada, 1977), or Fe-Al complexes also existed.

Without DCB treatment, quartz was detected in all Fe-nodules. Other clay minerals were not detected (Fig. 5.1a). After DCB treatment, the fine sand- and silt-size fractions of Fe nodules contained mainly quartz, wavellite, and/or carbonate-fluorapatite and were not shown. The clay size-fraction contained smectite, kaolinite, wavellite, and quartz (Fig. 5.1b). Results suggested that poorly-crystalline Fe-hydroxide and/or oxides might have bonded quartz, clay minerals, and phosphate minerals to form Fe nodules.

The onset of an endothermic DSC peak for Fe nodules occurred at about 250°C, but that of goethite occurs at about 300°C (Fig. 5.2). Therefore, the poorly crystalline Fe material of the nodules are less heat stable than goethite.

Results of sand grain counts of Fe nodules for the Lochloosa variant soil (Table 5.2) indicated that the A and E horizons contained few Fe nodules. Eluviation in these horizons probably reduced Fe levels and restricted Fe nodule

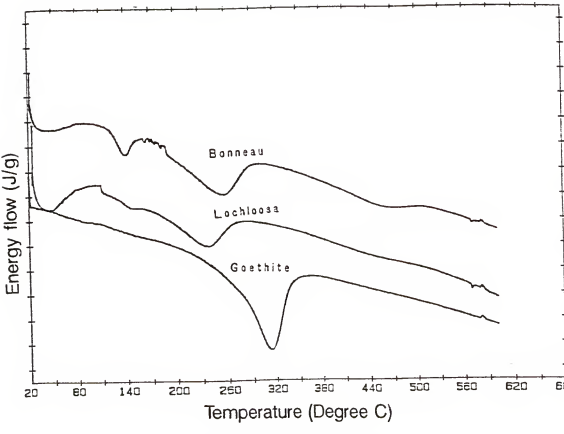

Fig. 5.2. Differential scanning calorimetry analysis for Fe nodules of Lochloosa variant (Btg1 horizon) and Bonneau variant (B/E horizon) soils and goethite.

Table 5.2. Number of Fe nodules (N), wavellite (W), and quartz (Q) per 100 counts in 1-2 mm (VCS), 0.5-1 mm (CS), and 0.1-0.25 mm (FS) size fractions in the profile of the Lochloosa variant soil.

Horizon	Depth	VCS			CS			FS		
		N	W	Q	N	W	Q	N	W	Q
	cm	---------- Count per hundred ----------								
Ap	0-18	-	-	-	0	1	99	0	0	100
E1	18-53	-	-	-	0	6	94	1	1	98
E2	53-79	-	-	-	1	1	98	1	0	99
BE	79-89	-	-	-	22	0	78	7	0	93
Btg1	89-137	67	21	12	22	4	74	8	0	92
Btg2	137-170	5	90	5	2	29	69	5	0	95
BCg	170-190	5	74	21	1	23	76	4	5	91
Cg	193-211	0	88	12	0	37	63	1	63	91

- No sand of 1-2 mm in size.

formation. Grain counts of Fe nodules were the highest in the B/E and Btg1 horizons and decreased in the C horizon. The other phosphatic soils showed similar trends. Mckeague (1981) also found that most P-rich nodules occurred in mottled albic horizons overlying argillic horizons of imperfectly or poorly-drained soils, and only some were in C horizons. Soil of the lower horizons (such as C horizon) may be below the water table and under reduced conditions most of the time. Iron under reducing conditions may be in ferrous form which is more soluble compared to ferric Fe. The ferrous Fe may be oxidized and precipitated when it moves upward as the water table rises into oxidized zones periodically. The precipitated Fe may coat on or cement the clay minerals, phosphate mineral, and quartz to form nodules. The DCB extractable-P values of the Fe nodules were so high that P must be associated with Fe; but the mechanism and nature of the association are uncertain.

5.3.2. Iron crystallinity and extractability in phosphatic and non-phosphatic soils

The effect of phosphorus on Fe crystallinity can be studied by comparing the extractability of Fe of the phosphatic soils and non-phosphatic soils which have different total P (Table 5.4). Goethite occurred in all the non-phosphatic soils, but was not detected in the phosphatic soils (Table 5.3). Hydroxy-interlayered vermiculite, kaolinite, and gibbsite occurred in both phosphatic and

nonphosphatic soils. In the nonphosphatic soils, these minerals occurred with goethite. Smectite, which restricted goethite formation (Schwertmann, 1988), did not occur with goethite in the non-phosphatic soils, but occurred in all the phosphatic soils except the Bonneau variant. The higher CEC of the phosphatic soils (except for the Bonneau variant) than that of the non-phosphatic soils was due to their higher clay contents and the presence of smectite. Base saturation and pH values varied from soil to soil in both the phosphatic and non-phosphatic soils.

The non-phosphatic soils have higher DCB-Fe but lower oxalate-Fe than the phosphatic soils (Table 5.4). Iron in the non-phosphatic soils was dominantly in the crystalline form (goethite), which was not extractable by oxalate. In the phosphatic soils, Fe was in poorly crystalline form and a significant fraction was oxalate-extractable (Wada, 1977). In the non-phosphatic soils, the DCB-Al was higher than the oxalate-Al. In the phosphatic soils, oxalate-Al was higher than DCB-Al. The phosphatic soils may have a high poorly crystalline Al content which may be more extractable by oxalate than by DCB. The oxalate may also dissolve more Al from wavellite and the clay minerals due to lower pH (pH 3.0) than does the DCB (near neutral). The oxalate-Al for the phosphatic soils was higher than that of the non-phosphatic soils indicating the presence of more noncrystalline Al. The DCB-Al varied from soil to soil in both phosphatic and non-phosphatic soils.

Table 5.3. Chemical and mineralogical properties of phosphatic and non-phosphatic soil horizons high in Fe content.

Soil	Horizon	Silt	Clay	O.C.	CEC	BS	pH	Clay mineral†
		--- g/kg ---			cmol/kg	%		
Non-phosphatic soils								
Fuquay	Btg2	93	189	0.8	3.4	6	5.0	I, K, Gi, Go
Lochloosa	Btg2	18	338	2.1	14.5	11	4.6	I, K, Go, Q
Pineda	Bo2	30	24	1.0	0.9	76	6.2	K, Go, Q
Vero	Btg1	30	258	14.9	11.8	39	4.6	I, K, Go, Q
Phosphatic soils								
Blichton	BCtg	67	609	0.8	56.5	23	4.5	S, I, K, Q
Bonneau variant	B/E	59	161	2.3	8.6	27	5.5	I, K, Q
Lochloosa variant	Btg1	106	190	0.7	22.0	25	5.1	S, K, Q
Norfolk	C	170	655	0.6	77.2	20	4.8	S, Q
Wabasso	Btg3	69	254	1.2	30.5	65	5.6	S, K, Q

† Go = goethite, Gi = gibbsite, I = Hydroxyl-interlayered vermiculite, K = kaolinite, Q = quartz, and S = smectite.

Table 5.4. Total P; oxalate-extractable P, Si, Fe, and Al; and dithionite-citrate-bicarbonate (DCB)-extractable P, Fe, and Al of phosphatic and non-phosphatic soils.

Soil	Horizon	Oxalate Si	P			Al		Fe	
			Total	Oxalate	DCB	Oxalate	DCB	Oxalate	DCB
			mmol/kg						
Non-phosphatic soils									
Fuquay	Btg2	5d†	9	0.4e	3.0g	30.9f	115.4b	3.2g	646c
Lochloosa	Btg2	3d	33	1.1e	5.8f	44.1e	51.7f	7.4g	328d
Pineda	Bo2	0e	3	0.5e	1.0h	0g	0h	2.0g	1848a
Vero	Btg1	0e	5	0.2e	1.8g	30.5f	103.1c	19.0f	1281b
Phosphatic soils									
Blichton	BCtg	18bc	239	35.7c	25.1de	155.7b	104.4c	117.1b	214g
Bonneau variant	B/E	5d	176	23.0d	24.1e	67.9d	66.0e	46.2e	273e
Lochloosa variant	Btg1	5d	299	94.7b	69.0a	150.5bc	86.2d	315.0a	319d
Norfolk	B/E	22b	222	33.9c	27.2c	221.0a	162.9a	95.6c	331d
Wabasso	Btg3	27a	334	151.5a	32.9b	148.1c	26.4g	78.9d	239f

† Data with the same lower case letter within columns are not significantly different at 0.05 level by Duncan's multiple range test.

The total P, oxalate-P, and DCB-P values of the five phosphatic soils were all much higher than those of the four non-phosphatic soils. In the phosphatic soils, the oxalate-P was higher than the DCB-P because the phosphatic soils contained carbonate-fluorapatite or wavellite which were more soluble by oxalate than by DCB (Table 5.1). In the non-phosphatic soils, the oxalate-P was lower than the DCB-P, indicating that P associated with goethite was extractable by DCB but not by oxalate.

The oxalate-extractable Si for the non-phosphatic soils was 5 mmoles/kg or lower. The results indicated that Si at these levels did not affect Fe crystallization and goethite formation. In the phosphatic soils, the oxalate-Si ranged from 5 (Bonneau variant) to 27 (Wabasso) mmoles/kg (Table 5.4). The oxalate-Si levels for the Lochloosa variant and Bonneau variant were similar to that of the non-phosphatic Fuquay soil. The levels of oxalate-P were higher than the oxalate-Si in the phosphatic soils. Regression analysis for both phosphatic- and non-phosphatic soils showed that Fe was linearly related to P but not to Si in oxalate extracts (Figs. 5.3 and 5.4). There was a higher linear relation between Al and Si than that between Al and P of oxalate extraction. Therefore, phosphorus may have been a factor in restricting Fe from forming goethite in the phosphatic soils. Silica was related to Al probably in allophane or allophane-like material.

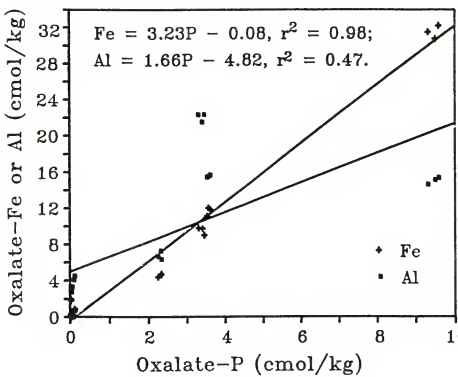

Fig. 5.3. Relation of Fe or Al to P in oxalate extracts for both phosphatic and non-phosphatic soils.

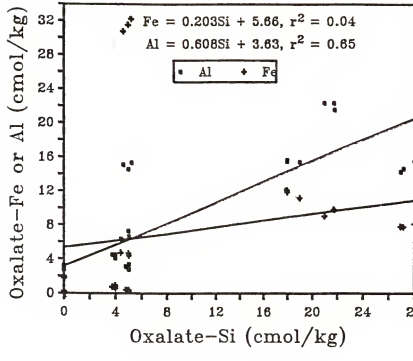

Fig. 5.4. Relation of Fe and Al to Si in oxalate extracts for both phosphatic and non-phosphatic soils.

Table 5.5. Mehlich I- and Olsen-extractable P of the phosphatic soils and the ratios of Mehlich I-P to total P (M-P/T-P) and Olsen-P to total P (O-P/T-P).

Soil	Horizon	Mehlich I-P	Olsen P	M-P / T-P	O-P / T-P
		----- mmol/kg ------		- per 1000 -	
		Contained Fe nodules			
Blichton	BCtg	2.51±0.01†	1.54±0.03	10.5	6.4
Bonneau variant	B/E	1.64±0.02	1.99±0.02	9.3	11.3
Lochloosa variant	Btg1	4.87±0.07	4.63±0.01	16.4	15.5
Norfolk	B/E	1.90±0.01	0.72±0.01	8.6	3.2
Wabasso	Btg3	50.23±0.51	4.84±0.16	150.4	14.5
		No Fe nodules			
Ocilla	Btg2	1.79±0.03	1.53±0.03	1.3	1.1

† Each mean and sample standard deviation value was from three observations.

5.3.3. Phosphorus extractability

Phosphorus in relation with noncrystalline Fe may be more extractable than P in crystalline P minerals. Only a small portion of the total soil P in all the phosphatic soils was extractable by Mehlich-I and Olsen extractants (Table 5.5). Among the five phosphatic soils containing Fe nodules, only the Lochloosa variant and Wabasso soils had higher Mehlich I-P and Olsen-P values than did the Ocilla variant soil which did not contain Fe nodules. However, the Ocilla variant soil had a higher total P (1382 mmol/kg) (Table 3.5). Mehlich I-P/Total P ratio and Olsen-P/Total P ratio of the Ocilla variant were lower than those of the other phosphatic soils containing Fe nodules. The high extractable P to total P ratios in the soils containing Fe nodules may be attributed to the noncrystalline Fe-P complex. The Mehlich I-P of the Wabasso soil which contained carbonate-fluorapatite was much higher than the Olsen P. Carbonate-fluorapatite-P was more extractable by Mehlich I than by Olsen extractant due to high acidity.

5.3.4. Phosphorus effect on goethite or hematite formation

Neutralization of ferric nitrate by NaOH produces ferric hydroxide and soluble salt including Na^+ and NO_3^- ions. Without removing salt, hematite and goethite formed after incubation at 80°C for 3 wks at initial pH 5.0 (Fig. 5.5b). When the salt from ferric hydroxide was removed, only goethite formed, as verified by XRD (Fig. 5.6a and b) with

both initial pH 5 and pH 12 treatments. Results suggest that salt allows both goethite and hematite formation. When P was added (Fe/P ratio = 10), formation of goethite was restricted or completely blocked depending on pH and salt content. At pH 5.0, the ferric hydroxide remained noncrystalline and dissolved completely in the oxalate reagent when salt was not removed (Fig. 5.5a and Table 5.6). When salt was removed, a large portion (807 g/kg) of Fe remained noncrystalline (Fig. 5.6c) and was oxalate extractable (Table 5.6). The small portion of Fe not extractable by oxalate was identified as goethite (Fig. 5.6d). At pH 12 and with salt removal, no goethite, hematite, or other Fe-P minerals formed when P was added. The precipitate gave a broad peak from 21 to 23° 2θ (d = 4.23-3.86 Å) by XRD (Fig. 5.6e). A large portion of Fe in the precipitate was extractable by oxalate (407 g/kg), which indicated a poorly or noncrystalline Fe material. The XRD peak position for the precipitates was similar to those of the Fe nodules from the phosphatic soils (Fig. 5.1a).

Without P addition, pH dropped from 5.0 to 3.2 when salt was removed. The drop in pH may be due to incomplete hydrolysis during ferric hydroxide preparation. The pH increased from 5.0 to 6.39 when P was added. The increase in pH may be due to the reaction

$$Fe(OH)_3 + H_2PO_4^- = Fe(OH)_2\ H_2PO_4 + OH^-.$$

At initial pH 12.0, the pH dropped to 10.3 when P was

Table 5.6. Effects of P, Al, Si, and clay minerals on ferric hydroxide crystallization and oxalate extractable Fe after incubation at 80°C for 3 wk.

Material added	Final pH	Fe_o/Fe_t†	Mineral formed
Initial pH 5.0, salt not removed			
None	2.56	0.02	Hematite+Goethite
KH_2PO_4	4.28	1.00±0	None
Initial pH 5.0, salt removed			
None	3.20	0.008±0.001h*	Goethite
Al	3.28	0.02±0.003g	Hematite
H_4SiO_4	4.88	0.836±0.003a	Hematite+Goethite
KH_2PO_4	6.39	0.807±0.003b	Goethite
Montmorillonite	4.09	0.41±0.001c	Hematite
Vermiculite	7.20	0.146±0.003f	Hematite
Kaolinite	4.25	0.203e	Hematite
Gibbsite	4.96	0.225±0.003d	Hematite
Initial pH 12, salt removed			
None	10.4	0.034±0g	Goethite
Al	12.0	0.204±0.003c	Hematite
H_4SiO_4	10.4	0.511±0.003a	None
KH_2PO_4	10.3	0.407±0.003b	None
Montmorillonite	10.4	0.195±0d	Goethite
Vermiculite	10.4	0.094±0.003f	Goethite
Kaolinite	10.5	0.098±0.001f	Goethite
Gibbsite	11.9	0.105±0.003e	Hematite

† Fe_o = Oxalate-extractable Fe; Fe_t = Total Fe.

* Data with the same low case letter are not significantly different at 0.05 level by Duncan's multiple range test.

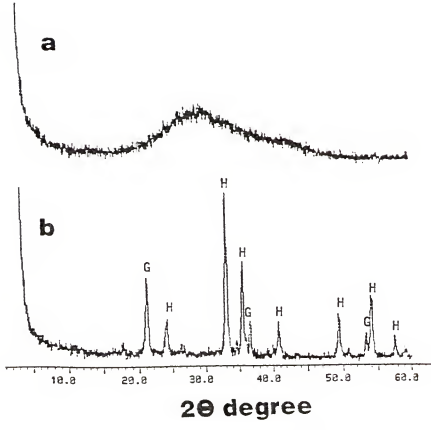

Fig. 5.5. Results of x-ray diffraction analyses of Fe materials after adjusting to pH 5.0 by NaOH and incubating for 3 wks at 80°C. (a) ferric nitrate + P and (b) ferric nitrate. G = goethite and H = hematite.

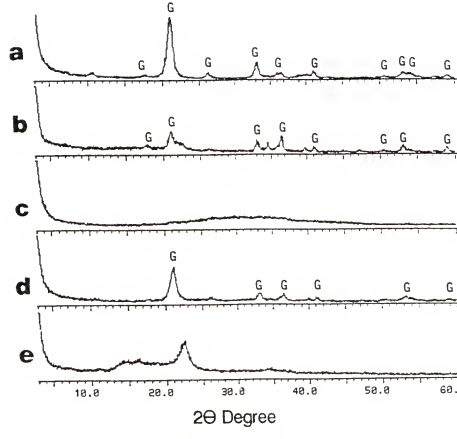

Fig. 5.6. Results of x-ray diffraction analyses of Fe materials formed from ferric hydroxide after 3 wks incubation at 80°C. (a) Fe at pH 5.0, (b) Fe at pH 12.0, (c) Fe+P at pH 5.0, (d) Fe+P at pH 5.0 and after oxalate treatment, (e) Fe+P at pH 12.0. G = goethite.

added and to 10.4 without P addition. The decrease in pH may be due to the buffering effect of P.

Ferric hydroxide became insoluble to oxalate after incubation at 80°C for 3 wks. The Oxalate-Fe/Total-Fe ratios for pH 5.0 and 12.0 treatments were 0.008 and 0.03, respectively, when salt was removed. The ratio was 0.02 when salt was not removed at pH 5.0 (Table 5.6). Results suggest that salt has little effect on Fe crystallization. However, salt does affect the species of Fe mineral formed.

The oxalate-Fe increased when ions or minerals were added (Table 5.6), indicating an inhibitory effect on Fe crystallization. The results supported the findings of some other authors (Schwertmann and Taylor, 1977; Schwertmann, 1988). Oxalate-Fe was much higher for P and Si, however, indicating that these ions were much more effective than Al and clay minerals in inhibiting crystallization. Goethite or hematite did form when Al or minerals were added at both pH 5.0 and pH 12.0. The crystalline Fe mineral did not form when P or Si was added at pH 12.0 (Table 5.6).

Similar to ferric hydroxide, a large weight loss for the Fe-P precipitates (initial pH 12) occurred at about 100°C; but the weight losses for goethite and hematite occurred at about 300°C. Weight loss for goethite (152 g/kg) was higher than the weight of its structural water content (101 g/kg). Hematite which does not contain structural water, lost 56 g/kg from 25 to 600°C. Apparently these

Table 5.7. Weight loss of the synthetic goethite, hematite, ferric hydroxide, and Fe-P complex at 600°C as determined by thermogravimetric analysis and the calculated water content from the molecular formula of ferric hydroxide ($Fe(OH)_3$), goethite (FeOOH), and hematite (Fe_2O_3).

Species	Initial temperature 25°C	110°C	Calculated water content
	Weight loss		
	---------- g/kg ----------		
Ferric hydroxide	241	126	253
Goethite	152	129	101
Hematite	56	51	0
Fe-P (pH 12)	147	56	-†

† Value cannot be calculated.

precipitates contained hydroxide in addition to goethite and hematite. The measured weight loss (147 g/kg) for the Fe-P material was less than that of goethite (Table 5.7). The results suggested that phosphate ions possibly replaced hydroxyl groups in ferric hydroxide, restricting goethite crystallization and rendering the material more extractable by oxalate. Parfitt et al. (1975) showed that two surface hydroxy ions (or water molecules) of β-ferric hydroxide or amorphous ferric hydroxide gel were replaced by one phosphate ion. Two of the oxygen atoms of the phosphate ion were coordinated, each to a different Fe^{+3} ion, resulting in a binuclear surface complex of the type $Fe\text{-}O\text{-}P(O_2)\text{-}O\text{-}Fe$.

5.4. Summary and Conclusions

Crystalline Fe minerals were not detected in the phosphatic soils although the DCB-Fe was relatively high. In contrast, goethite was detected in the non-phosphatic soils. Phosphate in the phosphatic soils has apparently restricted crystalline Fe mineral formation. This was confirmed by the results of laboratory incubation studies. Phosphate associated with Fe was in poorly crystalline form and was more extractable by Mehlich I and Olsen extractants compared to P in the well crystalline (wavellite) form.

CHAPTER 6
EFFECTS OF ORGANIC ACIDS AND CLAY MINERALS ON THE DISSOLUTION OF CARBONATE-FLUORAPATITE AND WAVELLITE

6.1. Introduction

A number of organic acids including oxalic, citric malic, malonic, succinic, lactic, formic, and phthalic acids have been identified in the organic fraction at A and E horizons of soils (Hue et al., 1986). Fox and Comerford (In review) found that oxalic acid concentration could be as high as 1-2 mmol/kg in soils. These low molecular-weight organic acids can complex or chelate polyvalent cations such as Al to form precipitated hydroxy-Al species in a non-crystalline state (Kwong and Huang, 1979; Violante and Violante, 1980). Organic anions are produced by micro-organisms during organic matter decomposition or by plant roots and may play an important role in increasing plant availability of P in soil (Earl et al., 1979). The mechanisms involve (i) competitive sorption reactions; (ii) dissolution of o-phosphate adsorbents by organic ligands; and (iii) modification of the surface charge on o-phosphate adsorbents by organic ligand adsorption (Traina et al. 1986). Aliphatic acids can be divided into three groups according to their Al complexing capacities: (i) citric and oxalic as strong complexers; (ii) malic and malonic as

moderate; (iii) lactic and succinic as weak. The strong complexers are favorable for the formation of stable 5- or 6-bond ring structures with Al (Hue et al., 1986).

Carbonate-fluorapatite and wavellite are common P minerals in the phosphatic soils of Florida. Total P contents were much lower in the surface horizons than those in the lower horizons (Chapter 3). Eluviation and removal by plants are important in reducing P of the eluvial horizon (Smeck, 1973). Weathering of P minerals is affected by pH (Joos and Black, 1950; Graham, 1955), topographic relief, ground water (Flicoteaux and Lucas, 1984), exchangeable Al (Chien et al., 1980), and Ca (Graham, 1955; McLean and Balam, 1967). Organic acids may also play an important role in the weathering of P mineral, especially in the surface soil in which organic acids were present (Hue et al., 1986).

The objective of this study was to evaluate the effect of organic acids, pH, and the presence of clay minerals on dissolution of carbonate-fluorapatite and wavellite.

6.2. Materials and Methods

Carbonate-fluorapatite from Bone Valley formation of central Florida and wavellite from Arkansas on sandstone provided by Burnham Petrographic Company were used in the study. Total P, Ca, Mg, Al, and Fe in carbonate-fluorapatite were 4.58, 7.13, 0.302, 0.229, and 0.046 mol/kg, respectively; and in wavellite, 3.15, 0.273, 0.233, 3.894, and 0.0585 mol/kg, respectively, as determined by Na_2CO_3

fusion method (Olsen and Summers, 1982). Both carbonate-fluorapatite and wavellite standards contained a small portion of quartz. Specimens were ground to pass a 0.1-mm sieve. Organic acids used included citric acid, oxalic acid, and formic acid.

6.2.1. Effects of organic acids at fixed pH

A 200.0-mg carbonate-fluorapatite sample or a 290.0-mg wavellite sample was weighed into a 125-ml Erlenmeyer flask containing 80-ml water or organic acid solution, so that each flask contained 0.91 mmoles of carbonate-fluorapatite-P or wavellite-P, or a total P concentration of 11.4 mmol/L. The concentrations of formic, oxalic, and citric acids were $3x10^{-2}$, $1.5x10^{-2}$, and 10^{-2} M, respectively. These concentrations provided equivalent carboxyl group concentrations for the three organic acids. The pH values of water, formic acid, oxalic acid, and citric acid were adjusted to 3, 4, and 5 with NaOH or HCl twice a week during incubation and at the end of incubation. Two drops of toluene were added to each flask to restrict microbial activity. The contents were incubated for 4 wks at 24±2°C. At the end of incubation, the volume for each treatment was recorded. The supernantant solution for each treatment was obtained after centrifugation at 3000 rpm for 15 min. The soluble P in the supernatant solution was determined (John, 1970). The portion of H^+ ions dissociated from carboxyl group of organic acids from pH 3.0 to 5.0 was calculated

using dissociation constants (K_A) of the three organic acids (Weast et al., 1984). The K_A for formic acid is 1.772×10^{-4}; the K_{1A} and K_{2A} for oxalic acid were 5.9×10^{-2} and 6.4×10^{-5}; and the K_{1A}, K_{2A}, and K_{3A} values for citric acid were 7.45×10^{-4}, 1.73×10^{-5}, and 4.02×10^{-7}, respectively.

6.2.2. Effects of organic acids with incubating time

Duplicate samples containing 100 mg of carbonate-fluorapatite or 145 mg wavellite were weighed into 50-ml centrifuge tubes, and aliquots of 40-ml organic acid solutions were added to each. Three organic acids at two concentrations were used. The concentrations of formic acid were 3×10^{-2} and 3×10^{-3} M, those of oxalic acid were 1.5×10^{-2} and 1.5×10^{-3} M and those of citric acid were 10^{-2} and 10^{-3} M. The lower and higher concentrations provided equivalent carboxyl group concentrations for the three organic acids.

The organic acids, as well as water, were adjusted to pH 3, 4, and 5, respectively, using NaOH or HCl. Two drops of toluene were added and the samples were incubated at 24±2°C for 1 wk, 4 wks, and 8 wks. The suspensions were mixed twice a week. At the end of incubation, the pH value was determined. The samples were then centrifuged at 3000 rpm for 15 min. The supernatant solutions were analyzed for P (John, 1970).

6.2.3. Effect of clay minerals

Carbonate-fluorapatite (50 mg) and wavellite (72 mg) samples were weighed in 50-ml centrifuge tubes. Portions (50

mg) of montmorillonite (<0.1μm), vermiculite (<50 μm), kaolinite (<2 μm), or gibbsite (<50 μm) were added; and 40-ml aliquots of water, citric acid (10^{-2} and 10^{-3} M), oxalic acid ($1.5x10^{-2}$ and $1.5x10^{-3}$ M), or formic acid solution ($3x10^{-2}$ and $3x10^{-3}$ M) were added. The pH for H_2O and organic acid solutions were adjusted to 3 and 4 using NaOH or HCl before adding to carbonate-fluorapatite or wavellite. The mixtures were incubated for 4 wks. The pH values at the end of incubation were determined. The samples were then centrifuged at 3000 rpm for 15 min. The supernatant solutions were analyzed for P by phosphomolybdic blue method (John, 1970) and Al by atomic absorption.

6.3. Results and Discussion

6.3.1. Effects of organic acids at fixed pH

The volumes of organic acid-P mineral suspensions ranged from 81 to 83 ml for both carbonate-fluorapatite and wavellite after incubation for 4 wk. The increase in volume was due to addition of HCl or NaOH during incubation for maintaining solution pH. In both water and organic acid solutions, the soluble P from carbonate-fluorapatite (Fig. 6.1a) was much higher than that from wavellite (Fig. 6.1b). Carbonate-fluorapatite, a Ca-P, was less stable under acidic condition compared to wavellite, an Al-P (Lindsay and Moreno, 1960).

Soluble P in water or organic acid solution decreased with increasing pH. The 0.91 mmoles carbonate-fluorapatite-P

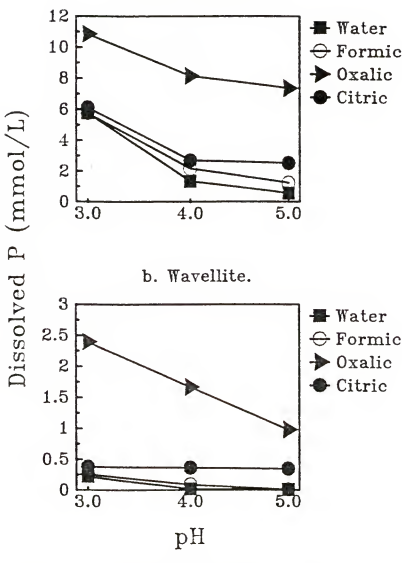

Fig. 6.1. Effects of organic acids on P dissolution from carbonate-fluorapatite and wavellite after incubation for 4 wks at 24±2°C under fixed pH condition. The solution concentration of formic, oxalic, and citric acids are $3x10^{-2}$, $1.5x10^{-2}$, and $1.0x10^{-2}$ M, respectively.

or wavellite-P originally used in the 81- or 83-ml solutions gave a total P concentration of 11 mmol/L. All the added carbonate-fluorapatite was soluble only in oxalic acid solution at pH 3.0. In oxalic acid solution of higher pH, or in water, formic acid, or citric acid at all three pH values, only portions of the incubated carbonate-fluorapatite-P were soluble (Fig. 6.1a).

The effects of organic acids on P solubility of carbonate-fluorapatite decreased in the order, oxalic acid > citric acid > formic acid > water (Fig. 6.1). The strong effect of oxalic acid on carbonate-fluorapatite dissolution may be due to insoluble Ca-oxalate formation which would reduce solution Ca resulting in more complete decomposition of carbonate-fluorapatite. Citric or formic acid can form complexes with Ca (Sposito and Mattigod, 1980). At pH 3.0, the amounts of soluble P in formic and citric acid solutions were only slightly different. As pH increased, soluble P in both solutions decreased. The soluble P decreased more rapidly in formic acid solution than in citric acid solution as pH increased. This can be due to higher H-ion dissociation from carboxyl groups and lower acidity in formic acid than in citric acid at pH 4.0 and 5.0 (Fig. 6.2).

In wavellite solutions, results showed that only a small portion of wavellite-P added was soluble in water and organic acids solutions at all the three pH values (Fig.

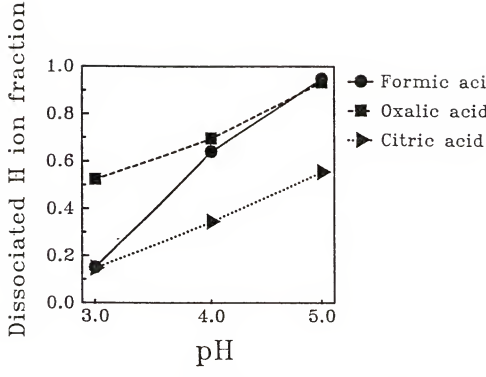

Fig. 6.2. The change in fraction of dissociated H^+ ion from the carboxyl group of organic acids with pH. The values were calculated from the dissociation constants of organic acids provided by Weast et al., (1984).

6.1b). Soluble P from wavellite also decreased as pH increased (Fig. 6.1b). It was much lower in formic acid solution than in oxalic acid solution because the formate ion was much less effective in complexing Al than the oxalate ion (Hue et al., 1986). At pH 5.0, soluble P in formic acid was not different from that in the water solution. In citric acid soluble P was higher than in formic acid, but was lower than in oxalic acid solution. The decrease was slight in citric acid solution with an increase in pH from 3.0 to 5.0.

6.3.2. Effects of organic acids with incubating time

Without controlling solution pH, the pH values of water and organic acid solutions all increased when carbonate-fluorapatite was added. Since the solution pH did not change much from 1 wk to 8 wk of incubation, only the pH values after 8-wk of incubation are shown (Fig. 6.3a). The increase in solution pH may be due to dissolution of carbonate-fluorapatite. The highest pH occurred in oxalic acid solutions due to Ca-oxalate precipitation, resulting in more complete carbonate-fluorapatite dissolution:

$$Ca_{10}(PO_4,CO_3)_6F_2 + 3H^+ + 9COOHCOO^- + 9H_2O = 9CaC_2O_4.H_2O + (6-x)H_2PO_4^- + xH_2CO_3 + CaF_2.$$

The pH values of water and organic solutions also increased with addition of wavellite (Fig. 6.3b), probably due to the

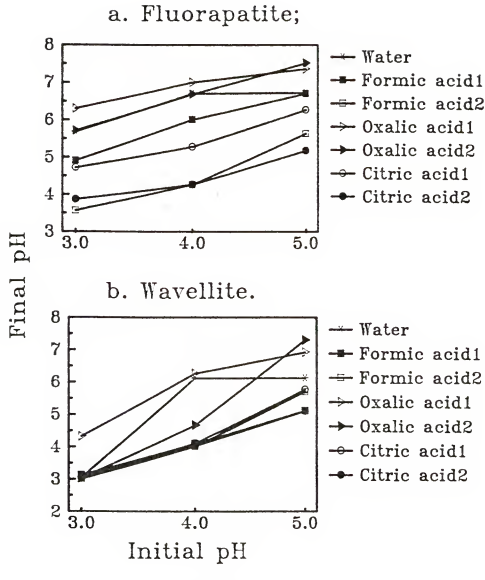

Fig. 6.3. The change in solution pH after 8-wk incubation of carbonate-fluorapatite or wavellite with water, formic acid, oxalic acid, or citric acid solutions. a. Carbonate-fluorapatite and b. wavellite. Concentrations for formic acid were $3x10^{-3}$ M (formic acid1) and $3x10^{-2}$ M (formic acid2); for oxalic acid, $1.5x10^{-3}$ M (oxalic acid1), and $1.5x10^{-2}$ M (oxalic acid2); and for citric acid, 10^{-3} M (citric acid1) and 10^{-2} M (citric acid2).

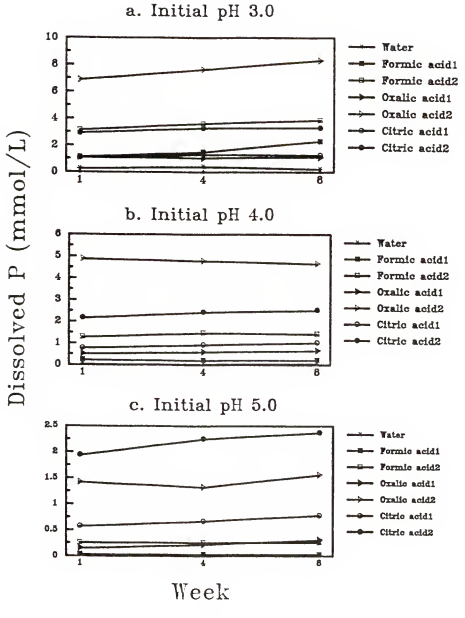

Fig. 6.4. Effects of organic-acid concentration, initial pH, and time of incubation on P solubility of carbonate-fluorapatite. Concentrations for formic acid were $3x10^{-3}$ M (formic acid1), and $3x10^{-2}$ M (formic acid2); for oxalic acid, $1.5x10^{-3}$ M (oxalic acid1), and $1.5x10^{-2}$ M (oxalic acid2); and for citric acid, 10^{-3} M (citric acid1) and 10^{-2} M (citric acid2).

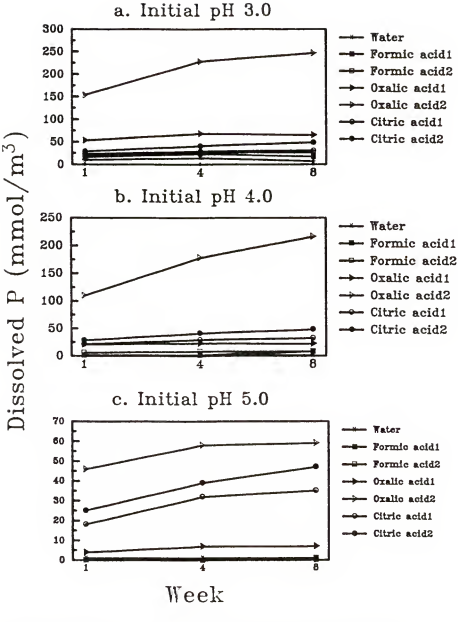

Fig. 6.5. Effects of organic-acid concentration, initial pH, and time of incubation on P solubility of wavellite. Concentrations for formic acid were $3x10^{-3}$ M (formic acid 1) and $3x10^{-2}$ M (formic acid 2); for oxalic acid, $1.5x10^{-3}$ M (oxalic acid 1), and $1.5x10^{-2}$ M (oxalic acid 2); and for citric acid, 10^{-3} M (citric acid 1) and 10^{-2} M (citric acid 2).

decomposition of wavellite and formation of stable $Al(OH)_2^+$ and $H_2PO_4^-$ ions:

$$Al_3(PO_4)_2(OH)_3.5H_2O + H^+ = 3Al(OH)_2^+ + 2H_2PO_4^- + 2H_2O.$$

However, the pH increases were not as great for wavellite as for carbonate-fluorapatite.

The effect of incubation on P solubility beyond 1 wk was not as pronounced as those of the initial solution pH and concentration of organic acid (Figs. 6.4 and 6.5. and Table 6.1). An increase in soluble P with incubation time occurred only in citric acid solutions and at the higher concentration of oxalic acid solution for both minerals. In water and formic acid solutions, a change in soluble P with incubation time was not evident.

The values of regression coefficients and R^2 of the stepwise regressions showed that, for both carbonate-fluorapatite and wavellite, the change in H^+ concentration has a relatively greater effect on dissolved P than organic acid concentration in formic acid solution (Table 6.1); but the reverse was true in oxalic and citric acid solutions. At initial pH of 3.0, considerable amounts of P were soluble in formic acid solution at both $3x10^{-2}$ M and $3x10^{-3}$ M concentrations; but the soluble P was very low at high pH (Figs. 6.4 and 6.5). At initial pH 5.0, no P was soluble from wavellite. The amount was very small from carbonate-fluorapatite in formic acid solution at both concentrations.

Table 6.1. Stepwise regression of dissolved P (P) (mmol L^{-1}) to H^+ ion concentration (H^+) (mmol L^{-1}), organic acid concentration (O.A.) (mmol L^{-1}), and time of incubation (wk).

Organic acid	Regression equations†	R^2	p>F
	Carbonate-fluorapatite		
Formic	$P = 0.223 + 1.636(H^+)$	0.408	0.0001
	$P = -0.315 + 0.147(O.A.) + 1.636(H^+)$	0.741	0.0001
Oxalic	$P = 0.149 + 0.446(O.A.)$	0.644	0.0001
	$P = -0.596 + 0.446(O.A.) + 2.015(H^+)$	0.774	0.0001
Citric	$P = 0.396 + 0.221(O.A.)$	0.864	0.0001
	$P = 0.183 + 0.221(O.A.) + 0.573(H^+)$	0.922	0.0001
	Wavellite		
Formic	$P = 0.013 + 0.177(H^+)$	0.774	0.0001
	$P = -0.008 + 0.005(O.A.) + 0.177(H^+)$	0.853	0.0001
Oxalic	$P = 0.103 + 0.134(O.A.)$	0.638	0.0001
	$P = -0.114 + 0.134(O.A.) + 0.587(H^+)$	0.758	0.0001
Citric	$P = 0.142 + 0.025(O.A.)$	0.529	0.0001
	$P = 0.078 + 0.025(O.A.) + 0.015(wk)$	0.600	0.0001

† Regression parameter with p value > 0.05 was excluded from the equation.

Therefore, the effect of formic acid on carbonate-fluorapatite and wavellite dissolution may be due to its acidity effect.

In citric and oxalic acid solutions, organic acid concentration was more closely related to soluble P than solution pH. The P solubility of wavellite by citric acid solution was not related to acidity between pH 3.0 and 5.0.

6.3.3. Effects of clay minerals

The pH values of the solutions of carbonate-fluorapatite-organic acid and wavellite-organic acid incubations were higher when clay minerals were added. Soluble P decreased in all organic acid-clay suspensions at initial pH 3.0 treatments (Table 6.2). The decrease in soluble P by clay additions may be due to (1) P retention by clay minerals; (2) acidity neutralization by clay minerals; and (3) interaction between organic acid and clay mineral. Negatively charged organic ions can be bound by clays through adsorption to positively-charge edges or exchange of structural OH groups (Lagaly, 1984).

Effects of clay mineral species on P solubility of carbonate-fluorapatite and wavellite were inconsistent (Table 6.2 and 6.3). The inconsistent results may be due to the following factors.

Dissolved P can be retained by clay minerals. The capacity of P retention by clay minerals decreased in the order: gibbsite > kaolinite > vermiculite and

Table 6.2. Soluble P from carbonate-fluorapatite after 4-wk incubation with water and organic acids in the presence of clay minerals.

Clay mineral	Final pH	Soluble P	Soluble Al	Final pH	Soluble P	Soluble Al
		-cmol m^{-3}-			-cmol m^{-3}-	
	Initial pH 3.0			Initial pH 4.0		
			Water			
None	5.5	32.4a†	0.0	6.9	2.4c	0.0
Montmorillonite	5.7	18.1e	0.0	7.5	4.7b	0.0
Vermiculite	6.5	20.3d	0.0	7.8	7.5a	0.0
Kaolinite	5.8	30.5b	0.0	6.9	2.1d	0.0
Gibbsite	5.8	26.8c	0.0	7.0	1.8e	0.0
			Formic			
None	5.7	79.4a	0.0	7.1	18.1a	0.0
Montmorillonite	7.1	44.2c	0.0	7.2	4.7c	0.0
Vermiculite	7.0	42.1c	0.0	7.6	5.3c	0.0
Kaolinite	7.0	68.6b	0.0	7.3	17.3a	0.0
Gibbsite	6.6	41.8c	0.0	7.3	14.0b	0.0
			Oxalic			
None	7.1	82.4a	0.0	7.7	35.3a	0.0
Montmorillonite	7.0	54.4b	5.0	7.6	23.2d	10.0
Vermiculite	7.1	63.6b	0.0	7.5	28.8c	2.3
Kaolinite	7.3	55.5b	0.0	7.6	33.7ab	2.3
Gibbsite	7.0	69.2b	0.0	7.6	32.4b	0.7
			Citric			
None	4.7	54.7a	5.8	5.5	48.1a	5.2
Montmorillonite	4.9	51.5b	94.4	6.1	37.7c	75.9
Vermiculite	6.3	41.3c	23.9	6.8	29.3d	18.8
Kaolinite	4.9	50.6b	12.4	5.6	41.8b	10.2
Gibbsite	5.0	54.6a	65.2	5.8	37.4c	67.7

† Data within column and solution with the same lower case letter was not significant different at $p < 0.05$ level by Duncan test.

Table 6.3. Soluble P from wavellite after 4-wk incubation with water and organic acids in the presence of clay minerals.

Clay mineral	Final pH	Soluble P	Soluble Al	Final pH	Soluble P	Soluble Al
		-cmol m^{-3}-			-cmol m^{-3}-	
		Initial pH 3.0			Initial pH 4.0	
			Water			
None	3.3	11.0a†	16.1	5.7	0.5d	0.0
Montmorillonite	3.8	2.8e	4.4	6.7	2.3b	3.0
Vermiculite	5.6	5.6c	3.7	7.5	4.9a	2.0
Kaolinite	3.2	8.7b	17.4	5.8	1.0c	0.0
Gibbsite	3.6	3.9d	27.2	5.9	1.1c	0.0
			Formic			
None	3.3	12.5a	17.8	4.2	1.7b	3.6
Montmorillonite	3.5	5.6c	13.8	7.0	2.0a	9.6
Vermiculite	6.5	5.1d	0.0	7.3	1.6b	0.9
Kaolinite	3.3	8.8b	14.8	6.9	1.5b	9.4
Gibbsite	3.5	5.5c	34.4	6.4	0.7c	0.0
			Oxalic			
None	4.1	50.7a	73.7	6.5	21.0a	38.1
Montmorillonite	5.6	11.3b	84.8	6.9	8.8c	78.5
Vermiculite	6.8	2.4d	18.6	7.2	4.7d	6.2
Kaolinite	5.0	14.7c	56.7	6.6	15.0b	42.0
Gibbsite	5.7	15.9c	71.5	6.7	14.1b	50.0
			Citric			
None	3.1	15.8a	21.0	4.3	15.3a	37.6
Montmorillonite	3.4	14.4ab	67.6	4.7	14.8a	60.0
Vermiculite	5.3	12.8b	68.8	6.5	14.3a	63.7
Kaolinite	3.2	15.4ab	25.0	4.4	14.3a	50.0
Gibbsite	3.3	14.3b	52.2	4.4	13.8b	52.8

† Data within column and solution with the same low case letter was not significant different at $p < 0.05$ level by Duncan test.

montmorillonite (Tisdale et al., 1985). Calcium dissolvedfrom carbonate-fluorapatite can displace H^+ ion from montmorillonite and vermiculite into the solution resulting in more carbonate-fluorapatite dissolution. However, vermiculite and montmorillonite may be more effective in neutralizing solution acidity than kaolinite and gibbsite, resulting in most cases in higher solution pH and lower P solubility (Tables 6.2 and 6.3). The pH values of vermiculite, montmorillonite, kaolinite, and gibbsite suspensions in water (v/w ratio of 800) were 8.1, 7.5, 5.05, and 6.08, respectively. When 0.1 mmoles of HCl were added, the pH for the suspensions were 3.96, 3.24, 3.02, and 2.95, respectively. In oxalic and citric acid solutions, soluble Al was higher with montmorillonite than with other clay minerals (Tables 6.2 and 6.3). The Al in montmorillonite may be more soluble than other clay minerals by organic acids due to smaller particle size (<0.1 μm). The interaction between organic acid and Al from montmorillonite would reduce the activity of organic acids and thereby their effectiveness in dissolving phosphate minerals. However, Yuan (1980) showed that the interaction between Al and organic acids was not as strong as between Al and P.

At initial pH 4.0, soluble P was reduced by clay minerals in organic acid solutions. In water solutions, vermiculite and montmorillonite increased P solubility, but kaolinite and gibbsite had little effect. Vermiculite and

montmorillonite tended to maintain soluble P at > 2 cmol m^{-3} level.

6.4. Conclusions

Carbonate-fluorapatite was more soluble than wavellite over a pH range of 3.0 to 5.0 by water, formic acid, oxalic acid, and citric acid. The effects of acid on solubility of P minerals decreased in the order, oxalic > citric > formic > water. Soluble P decreased more rapidly with pH increase in formic acid suspensions than in citric acid and oxalic acid suspensions. Soluble P from carbonate-fluorapatite and wavellite reached maximum levels at one wk incubation at both levels of formic acid solutions ($3x10^{-2}$ and $3x10^{-3}$ M) and at the lower level of oxalic acid solution ($1.5x10^{-3}$ M). At the higher oxalic acid level ($1.5x10^{-2}$ M) and both citric acid levels (10^{-2} and 10^{-3} M), soluble P increased with time beyond initial wk. The solubility of P minerals by organic acids decreased when clay minerals were added; but in water suspensions at initial pH of 4.0, which contained very low soluble P, vermiculite and montmorillonite tended to maintain soluble P at > 2 cmol m^{-3} level. Results suggested that organic acids can enhance the release of P from carbonate-fluorapatite and wavellite in soils. Further study may elucidate the extent and plant-nutritional significance of P release through such a mechanism.

CHAPTER 7
FRACTIONATION OF INORGANIC PHOSPHORUS FOR
FLORIDA PHOSPHATIC SOILS AND PHOSPHATE MINERALS

7.1. Introduction

In characterization of inorganic P forms in soils, NH_4F which extracts P predominantly from Al-P (Turner and Rice, 1952) was used to distinguish Al-P from Fe-P (Chang and Jackson, 1957). But NH_4F extractable-P can underestimate Al-P in soils containing Fe-oxides, which can retain P released from Al-bound forms (Khin and Leeper, 1960; Fife, 1962). In calcareous soil or sediment, NH_4F extractable-P also underestimates Al-P (Williams et al., 1971). At present, there is no completely satisfactory P fractionation scheme which differentiates Al-P from Fe-P. The DCB removes Fe-P and reductant soluble P and has little effect on crystalline Al-P (Chang and Jackson, 1957), but the effect of DCB on noncrystalline Al-P solubility was not well known. Phosphate minerals containing both Ca and Al, such as crandallite $[CaAl_3(PO_4)_2(OH)_5.3H_2O]$, occur in Florida phosphatic soils. The extractability of these phosphate minerals by different P extractants is not known.

The objectives of the study were to examine the effectiveness of DCB in differentiating Fe-P from Al-P and

to test the extractability of P in phosphatic soils and P minerals by common chemical extractants.

7.2. Materials and Methods

Synthetic and natural phosphate minerals and those from phosphatic soils were used to compare extractabilities by different chemical reagents.

Artificial preparation of P phases was accomplished using the following procedures:

Iron-P: A 600-ml solution containing 10 ml of 1 M $FeCl_3$ and 30 ml of M NaH_2PO_4 was digested at boiling temperature on a hot plate for 3 days. Water was added frequently to maintain the solution volume during digestion. The precipitate was washed with water twice, centrifuged, and air-dried. The precipitate contained phosphosiderite ($FePO_4.2H_2O$) (Fig. 7.1). The maximum peak intensity occurred at d = 4.39 Å (hkl = 002) instead of 2.81 Å (hkl = 013 and 122). Three x-ray diffraction (XRD)-peaks with d = 5.45, 5.0, and 3.07 Å did not match well with those of phosphosiderite in PDF file 15-390. After air-drying, total P and Fe were determined to be 525 and 498 cmol/kg, respectively.

Aluminum-P: A 600-ml solution containing 30 ml of 1 M $AlCl_3$ and 90 ml of 1 M NaH_2PO_4 was boiled on a hot plate overnight. Water was added frequently to maintain the volume during digestion. The precipitate was washed with water twice, centrifuged, and air-dried. The precipitate contained

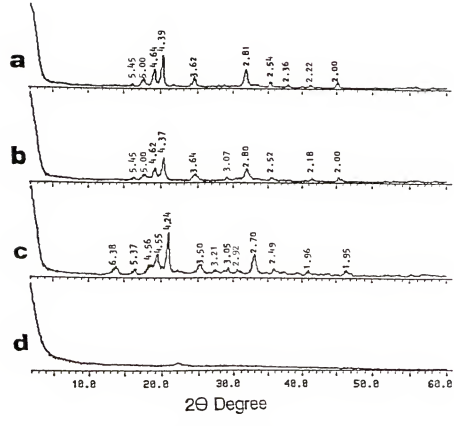

Fig. 7.1. Mineralogy of synthetic phosphates determined by x-ray diffraction. a. Fe-P (phosphosiderite), b. Fe-Al-P, c. Al-P (variscite), and d. noncrystalline Al-P. The numbers are d-spacing (Å).

variscite ($AlPO_4.2H_2O$) (Fig. 7.1). After air-drying, total P and Al were determined to be 633 and 589 cmol/kg, respectively.

Iron-Al-P: A 600-ml solution containing 15 ml of 1 M $AlCl_3$, 15 ml of 1 M $FeCl_3$ and 90 ml of 1 M NaH_2PO_4 was boiled on a hot plate for 3 days. The precipitate was washed with water twice, centrifuged, and air-dried. The precipitate contained phosphosiderite (Fig. 7.1). After air-drying, total P, Al, and Fe were determined to be 551, 159, and 353 cmol/kg, respectively.

Noncrystalline Al-P: A 250-ml solution was prepared by mixing 40 ml of 1 M $AlCl_3$ with 20 ml of 1 M NaH_2PO_4 and bringing to volume with distilled H_2O. The suspensions were adjusted to pH 7.0 by NaOH and centrifuged to remove supernatant solution. The precipitate was washed with saturated NaCl to remove soluble P, and then with water twice to remove salt. The precipitate was air-dried. The precipitate was noncrystalline with only one broad XRD-peak (d = 4.04 Å) (Fig. 7.1), containing 3.58 mol P/kg and 6.30 mol Al/kg.

Naturally occurring P minerals used in this study were carbonate-fluorapatite from central Florida Pliocene geologic strata (< 0.1 mm), Variscite-(<0.1 mm) provided by Minerals Unlimited Company, and wavellite (<0.1 mm) from Arkansas on sandstone provided by Burnham Petrographic Company.

Table 7.1. Total P, Al, and Ca; dithionite-citrate-bicarbonate-extractable (DCB)-Fe; and sample size for P fractionation.

Sample	P	Al	Ca	DCB-Fe	Sample† size
	----------	cmol/kg	----------		mg
Synthetic materials					
Al-P	633±21	589±15	0	0	100
Al-Fe-P	551±2	159±1	0	353	117
Fe-P	525±6	0	0	498	123
Noncrystalline Al-P	358±2	630±5	0	0	180
Natural minerals					
Flourapatite	458±2	18±3	689	7	141
Wavellite	313±4	390±2	30	5	205
Variscite	565±7	586±3	0	0	114
Soil materials					
Wauchula silt	171±1	415±4	65	52	378
Chobee silt	91±1	278±11	174	28	712
Chobee clay	83±1	285±2	126	22	777
Ocilla variant clay	109±2	589±3	7	9	592
Ocilla variant silt	239±1	437±9	0	20	270
Lochloosa variant					
Fe nodules	52±1	144±1	0	174	1234
silt	82±1	208±0	0	95	789
clay	74±1	456±4	0	39	873

† The sample size provided 20 mg P.

Soil materials used in this study were the silt and clay fractions from the Cg horizon (106-203 cm) of Chobee sandy clay loam from DeSoto County, containing carbonate-fluorapatite; the silt fraction from the Btg2 horizon (127-147 cm) of Wauchula fine sand from Polk County, containing crandallite; the silt and clay fractions from the Btg2 horizon (127-175 cm) of the Ocilla variant loamy fine sand from Union County; and Fe-nodules, silt, and clay fractions of the Btg1 horizon (89-137 cm) from the Lochloosa variant fine sand from Alachua County, containing wavellite.

Total P, Al, and Ca of the samples were determined by sodium carbonate fusion (Olsen and Summers, 1982) (Table 7.1). Total free Fe was determined by dithionite-citrate-bicarbonate (Mehra and Jackson, 1960).

The effectiveness of two fractionation schemes (I and II) which differentiate Fe-P from Al-P was tested. The procedure for scheme I was as follow:

(1) NH_4Cl-soluble P: Samples containing 20 mg P were weighed and transferred to a 100 ml polypropylene centrifuge tube. A 50-ml aliquot of 1 M NH_4Cl was added. These tubes were shaken for 30 min and centrifuged at 2000 rpm for 10 min. The supernatant solution was saved for analysis.

(2) DCB-extractable P, which includes Fe-P and reductant-soluble P (RS-P): A 40-ml aliquot of 0.3 M sodium citrate, a 5-ml aliquot of 1 M bicarbonate solution, and 1 g $Na_2S_2O_4$ were added to the sample residue from (1) above.

Table 7.2. Outline of fractionation schemes showing reagents, sequence of extraction, and conditions (all extractions performed at room temperature, unless otherwise stated).

Reagents, sequence of extraction and condition	Fractionation scheme I	II
NH_4Cl, 1 M, 30 min.	X	X
DCB, 85°C, 15 min.	X	-
NH_4F, 0.5 M, pH 8.2, 24 h	-	X
NaOH, 0.1 M, NaOH, 1 M, 17 h	X	X
DCB, 85°C, 15 min.	-	X
H_2SO_4, 0.5 N, 1 h	X	X

These samples were well mixed, heated to 85°C for 15 min in water bath, and centrifuged at 2500 rpm for 15 min. The supernatant solution was saved for analysis.

(3) NaOH-extractable P: The residue from (2) was washed twice with 25-ml saturated NaCl and centrifuged for 10 min. The supernatant solution was discarded. A 50-ml aliquot of solution containing 0.1 M NaOH and 1 M NaCl was added. These samples were shaken for 17 h, and centrifuged at 2500 rpm for 15 min. The supernatant solution was saved for analysis.

(4) H_2SO_4-extractable P: The residue from (3) was washed twice with 25 ml saturated NaCl and centrifuged for 10 min. The supernatant solution was discarded. A 50-ml aliquot of 0.5 N H_2SO_4 was added. These samples were shaken for 1 h and centrifuged. The supernatant solution was saved for analysis.

The procedure of scheme II was similar to the scheme B in Williams et al (1971), except that 0.5 N H_2SO_4 was used instead of 0.5 M HCl. Differences between schemes I and II are summarized in Table 7.2.

Soil and P mineral samples containing 20 mg P were also analyzed for extractable P by individual NH_4F, NaOH, and H_2SO_4 reagents. Samples were also analyzed for extractable P by double extraction using DCB reagent. The reagents used were the same as used in fractionation studies. Phosphate released by different extractants was determined by phosphomolybdic blue method (John, 1970).

7.3. Results and Discussion

7.3.1. Effect of Dithionite-citrate-bicarbonate

Two DCB extractions were made. The first extraction dissolved all 20 mg P and all Fe of synthetic Fe-P (phosphosiderite) by reducing ferric Fe. For the Fe-Al-P (Al substituted phosphosiderite), 19.16 mg P was released from the first DCB extraction although the material contained a considerable amount of Al (159 cmol/kg). The results suggested that DCB may dissolve P minerals which contain both Fe and Al. After the second DCB extraction, a small amount of Fe still remained as evidenced by a reddish color in the residue. From the Fe nodules and high Fe-containing silt and clay fractions of Lochloosa variant, more P was released by the first DCB extraction (Fig. 7.2) than from those of other soils. The fact that Fe nodules, silt fraction and clay fraction had both Fe and DCB-P in decreasing order suggests that DCB-P is closely related with Fe. The DCB-Fe contents of Fe nodules, silt, and clay of Lochloosa variant were very high. The first DCB extraction removed only 8.10, 6.25, and 4.95 mg P from the Fe-nodules, silt, and clay, respectively. The residue remained a reddish color after the first DCB extraction. The second DCB extraction removed additional 2.21, 1.85, and 1.2 mg P from these fractions, respectively (Fig. 7.2).

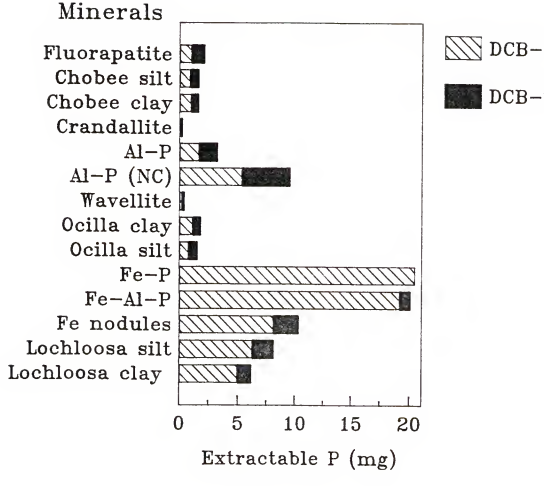

Fig. 7.2. Phosphorus extractability of P minerals and soils with 20 mg total P by dithionite-citrate-bicarbonate (DCB) extractions. DCB-1 = first extraction, and DCB-2 = second extraction. Al-P (NC) is noncrystalline Al-P.

Negligible amounts of P were extracted from natural wavellite and variscite by DCB (Fig. 7.2). The Ocilla variant soil, which contained wavellite but low Fe, also released low P by DCB extraction. The synthetic crystalline Al-P had more extractable P than natural variscite or wavellite, but less than noncrystalline Al-P which released 5.32 and 4.21 mg P in the first and second extractions from 20 mg P, respectively (Fig. 7.2). Little P was obtained from DCB extraction of crandallite, carbonate-fluorapatite, and Chobee silt and clay which contained carbonate-fluorapatite. The extractability of mineral-P by DCB decreased in the order Fe-P > Fe-Al-P > noncrystalline Al-P > Al-P > carbonate-fluorapatite > wavellite and variscite > crandallinte.

7.3.2. Effect of NH_4F

The NH_4F has been reported to extract Al-P but not Fe-P (Turner and Rice, 1952, Chang and Jackson, 1957). Extractability varied with Al-P minerals. Almost all the 20 mg P from the synthetic Al-P was extractable by NH_4F and only 3.17 and 7.62 mg P were extractable from natural variscite and wavellite, respectively (Table 7.4). The synthetic Al-P may have smaller particle size and therefore, may dissolve at a faster rate than the natural Al-P. More P (8.2 to 8.7 mg P) was extractable from the clay and silt of the Ocilla variant soil which contained wavellite by NH_4F than from natural wavellite. This may be

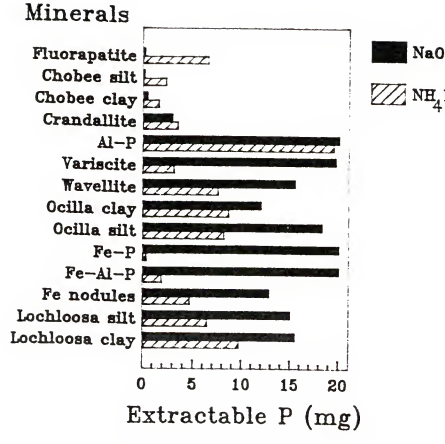

Fig. 7.3. Comparison of P extractability of different P minerals and soils containing 20 mg total P by 0.1 N NaOH and 1 N NH_4F.

due to both crystallinity and smaller particle size of Ocilla silt and clay than the ground wavellite mineral (<0.1 mm). For the Lochloosa variant soil, which also contained wavellite, NH_4F-extractable P increased from Fe nodules to silt to clay (Table 7.4); but total Fe decreased from Fe nodules to clay (Table 7.1). Therefore, the portion of Fe-P not extractable by NH_4F may increase from clay to Fe nodules. The NH_4F extracted a considerable amount of P (3.52 mg) from the crandallite silt of Wauchula soil. The NH_4F extractable P of crandallite was lower, however, than that of wavellite or the synthetic crystalline Al-P. The NH_4F extracted only 0.43 mg P from the synthetic Fe-P; however, it extracted some P from the natural carbonate-fluorapatite and soil samples containing this mineral (Table 7.4). The dissolution of carbonate-fluorapatite-P by NH_4F may be due to formation of calcium fluoride.

7.3.3. Effect of NaOH

The NaOH extracts P in both Al (Yuan and Fiskell, 1959) and Fe forms and has very little effect on carbonate-fluorapatite-P (Chang and Jackson, 1957). All 20 mg of synthetic Al-P, Fe-Al-P, and Fe-P were removed by NaOH. Large portions of P from natural variscite, wavellite, and soil materials containing wavellite were also removed by NaOH (Fig. 7.3). A negligible amount of P from the carbonate-fluorapatite and Chobee silt and clay was released by NaOH (Fig. 7.3). Therefore, NaOH is a satisfactory

extractant for Al- and Fe-P without affecting Ca-P. However, NaOH released little P from crandallite silt, a Ca-Al-P, from the Wauchula soil.

7.3.4. Effects of H_2SO_4

Acid-extractable Ca-P appears to give a reliable estimate of nonoccluded apatite. The H_2SO_4 was very effective in extracting Ca-P. All or almost all the 20 mg P in carbonate-fluorapatite and Chobee silt and clay was removed by H_2SO_4 (Fig. 7.4). It is not surprising because the P mineral in Chobee soil was mainly carbonate-fluorapatite which dissolves in acid. Less than 2 mg P from the synthetic phosphosiderite and variscite and natural variscite and wavellite were extracted by H_2SO_4 (Fig. 7.4). The H_2SO_4 extractable P for the clay and silt of Lochloosa variant soil was higher than that of Ocilla variant soil (Fig. 7.4). The higher extractable P in Lochloosa variant soil may be due to the presence of more poorly crystalline Fe-P or Al-P. The H_2SO_4 extractable-P for crandallite was much lower than that of carbonate-fluorapatite, but was higher than those of Al- and Fe-P minerals (Fig. 7.4).

7.3.5. Evaluation of the phosphate fractionation schemes

The DCB-P was much higher when the DCB extraction was followed by the NH_4F and NaOH extractions than for cases when DCB extraction was preceded by NaOH and NH_4F extractions for the Fe-P, Fe-Al-P, and Fe-nodules, silt, and clay of Lochloosa variant soil (Table 7.3 and 7.4). The DCB

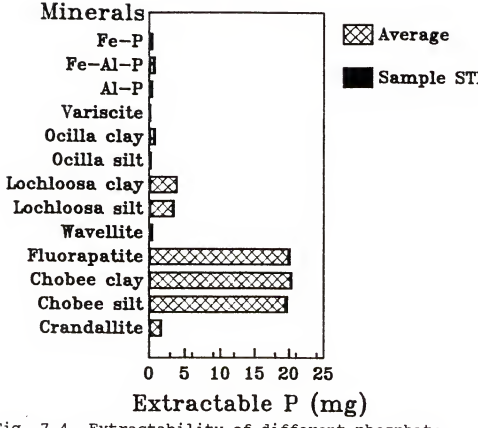

Fig. 7.4. Extractability of different phosphate minerals and soils containing 20 mg total P by 0.5 N H_2SO_4. Sample STD is sample standard deviation.

P following NaOH extraction was similar to RS-P (Chang and Jackson, 1957); while the DCB-P preceding NaOH extraction included Fe-P, RS-P, and noncrystalline Al-P. Since DCB extracted considerable amounts of noncrystalline Al-P, the subsequent NaOH extraction may underestimate the Al-P in scheme I.

The DCB-P levels from carbonate-fluorapatite and silt and clay fractions of Chobee soil were also higher before NH_4F and NaOH pretreatments than those after the sequential extraction by NH_4Cl, NH_4F, and NaOH (Table 7.3 and 7.4).

Crandallite, a Ca-Al-P and in the silt fraction of Wauchula soil, was not extractable by DCB (Table 7.3). However, when the DCB extraction followed NH_4F and NaOH extractions, 1.71 mg P was released (Table 7.4).

In scheme I, the coating of Fe oxide and/or hydroxide was removed from the Al-P and Ca-P. Therefore, the subsequent NaOH and H_2SO_4 extractions included the occluded Al-P and Ca-P. Almost all the residual P of variscite (20.1 mg P) and synthetic Al-P (18.3 mg P) from DCB extraction was removed by NaOH in scheme I (Table 7.3). For the Lochloosa variant, lower NaOH-P for Fe nodules than for clay resulted from the previous removal of the Fe-P in nodules by DCB extraction.

In scheme II, NH_4F and NaOH were used to extract Al-P and Fe-P, respectively. Iron-P in the silt fraction and Fe nodules, not extractable by NH_4F, was released by the

Table 7.3. Extractable P from samples with 20 mg total P for P fractionation scheme I.

Sample	Extractable P				
	NH_4Cl	DCB	NaOH	H_2SO_4	Total
	mg				
Al-P	0.10	1.68±0.10	18.30	-†	20.08
Fe-P	0.03	20.47±0.17	-	-	20.50
Fe-Al-P	0.07	19.16±0.13	0.87±0.04	0.03±0.02	20.13
Flourapatite	0.08	1.03±0.02	0.11	18.95	20.17
Wavellite	0	0.24±0.01	15.23±0.07	0.01	15.48
Variscite	0.02	0.17±0.07	20.12±0.23	0.01	20.32
Crandallite	0	0.15±0.00	1.19±0.15	1.52±0.01	2.86
Chobee silt	0.01	0.91±0.01	0.24±0.03	18.54±0.80	19.70
Chobee clay	0.03	0.99±0.04	0.34±0.01	18.64±0.24	20.00
Ocilla variant					
silt	0.01	0.79±0	17.28±0.09	0.06±0.01	18.14
clay	0	1.15±0.16	10.21±0.10	0.21±0.02	11.57
Lochloosa variant					
Fe nodules	0.01	8.10±0.07	7.55±0.23	0.40±0.03	16.06
silt	0.01	6.25±0.08	9.95±0.11	0.07±0.01	16.28
clay	0	4.95±0.05	11.04±0.25	0.16±0.01	16.15

† - is no residue left from the previous extraction.

Table 7.4. Extractable P from samples with 20 mg total P for P fractionation scheme II.

Sample	Extractable P†				
	NH_4F	NaOH	DCB	H_2SO_4	Total
	mg				
Al-P	19.56±0.07	0.42±0.01	-‡	-	20.08
Fe-P	0.43±0.01	19.00±0.07	0.57	-	20.03
Fe-Al-P	1.97±0.01	17.68±0.10	0.41	-	20.13
Flourapatite	6.58±0.49	0	0.61±0.01	13.35±0.38	20.62
Wavellite	7.62±0.34	9.15±0.54	0.18	0	16.95
Variscite	3.17±0.29	17.35±0.50	0.08±0.04	0	20.02
Crandallite	3.52±0.20	1.78±0.11	1.71±0.24	1.02±0.18	10.03
Chobee silt	2.37±0.04	0.04±0	0.50±0.02	17.63±0.24	20.55
Chobee clay	1.67±0.08	0.08±0.01	0.45±0.03	18.42±0.09	20.65
Ocilla variant					
silt	8.23±0.78	9.60±0.76	0.07	0.02	17.93
clay	8.70±0.13	2.47±0.07	0.19	0.16±0.01	11.52
Lochloosa variant					
iron nodules	4.74±0.19	8.56±0.16	2.42±0.03	1.22±0.10	16.95
silt	6.46±0.63	9.48±0.47	1.40±0.22	0.30±0.01	17.65
clay	9.78±0	6.42±0.05	0.44±0.01	0.26±0.01	16.90

† The NH_4Cl extractable P values for scheme II were the same as those of the scheme I and were not shown.
‡ - No residue left from the previous extraction.

subsequent NaOH extraction. But P in variscite and wavellite, which were only partially extractable by NH_4F, was also released by the subsequent NaOH extraction. Therefore, NaOH in scheme II extracted both Fe-P and Al-P. This could occur commonly in the phosphatic soils which contained high Al-P. NaOH is generally more efficient than NH_4F in removing Al-P (Fig. 7.3). The NaOH also released more P than NH_4F from the silt and clay fractions of Ocilla variant and Lochloosa variant soils. NaOH released very little P from the carbonate-fluorapatite sample, but NH_4F removed a considerable amount of P from it. In scheme II, underestimation of Al-P by NH_4F extraction can occur in soils containing Fe oxide (Fife, 1962) or in calcareous sediments (Williams et al., 1971).

All the residual P in carbonate-fluorapatite and in Chobee silt and clay in both scheme I and II was removed by H_2SO_4. More P from carbonate-fluorapatite was extracted by H_2SO_4 in scheme I than in scheme II, where NH_4F extraction was used (Tables 7.3 and 7.4). In both schemes, almost all the P from Al-P, Fe-P, Fe-Al-P, and variscite was removed by the preceding extractions, and no P was left for H_2SO_4. Little P from the natural wavellite or from the clay and silt of the Ocilla variant and Lochloosa variant soils was extracted by H_2SO_4 in both schemes, although the residues still contained over 1 mg P.

The sums of extractable P by different extractants in both schemes for wavellite and clay, silt, and Fe nodules containing wavellite were less than the total P (20 mg); but no wavellite was detected by XRD from the residues. The results were in

agreement with the findings of other authors (Yuan et al., 1960; and Syers et al; 1969) that total soil P can not be removed after sequential extractions. Low P recovery from silt and clay fractions may be due to the presence of P in the clay lattice and/or orthophosphate associated with extensively developed crystalline secondary Fe- and Al-containing components which can be extracted only after Na_2CO_3 fusion (Syers et al., 1969). Crandallite was detected in the residue of natural wavellite from both schemes by XRD, although it was not detected before the sequential extraction. The presence of crandallite in the residue of the natural wavellite accounted for the low recovery.

Crandallite-P was much less extractable by DCB, NaOH, and H_2SO_4 compared to P minerals in which P is associated with only one cation (i.e. Fe, Al, or Ca) (Fig. 7.3 and 7.4). The XRD analysis indicated that crandallite in the Wauchula silt was still present after the sequential extraction by scheme II. The ratio of XRD peak intensity of crandallite (d=2.95 nm) to quartz (d=3.343 nm) were 0.441 and 0.106, respectively, before and after the sequential extraction.

7.4. Conclusions

DCB extracted most Fe-P and RS-P, and had little effect on crystalline Al-P (variscite and wavellite) and Ca-P (carbonate-fluorapatite). However, DCB extracted a considerable amount of synthetic noncrystalline Al-P. Therefore, DCB is poor in differentiating Fe-P and Al-P in soils which contain both noncrystalline Fe-P and Al-P. The extractability of mineral-P by

DCB decreased in the order Fe-P > Fe-Al-P > noncrystalline Al-P >Al-P > carbonate-fluorapatite > wavellite and variscite > crandallite. The extractability of Al-P by NH_4F depends on the mineral species. More P from the synthetic Al-P and wavellite was extracted than from variscite. A considerable amount of P was also extracted by NH_4F from carbonate-fluorapatite, probably as a result of CaF_2 formation. NaOH is more effective in extracting Al-P than NH_4F, but is less effective in extracting Ca-P. H_2SO_4 extracted a large amount of carbonate-fluorapatite-P but a small amount of Al-P and Fe-P. Crandallite, an Al-Ca-P mineral, was only partially extractable by DCB, NH_4F, NaOH, and H_2SO_4.

The DCB, NaOH, and H_2SO_4 were used to extract Fe-P, Al-P, and Ca-P, respectively, in scheme I; but in scheme II, NH_4F, NaOH, DCB, and H_2SO_4 were used to extract Al-P, Fe-P, RS-P, and Ca-P, respectively. Phosphate in silt and clay fractions of Ocilla variant and Lochloosa variant was not completely removed by the sequential extractions of both schemes, indicating the presence of more resistant P material. Resistance to P extraction by crandallite, in which P is associated with both Ca and Al, suggests that similar resistance by soils may be attributable to more complex and (as yet) uncharacterized forms of P. Scheme I may underestimate Al-P and overestimate Fe-P in soil containing noncrystalline Al-P which can be dissolved by DCB. Scheme II may also underestimate Al-P and overestimate Fe-P since NH_4F is not effective in dissolving some Al-P such as P in natural variscite which is subsequently removed by NaOH. The Ca-P in scheme II may

be underestimated because NH_4F extracts carbonate-fluorapatite-P to some extent. Therefore, either scheme is not satisfactory in soil inorganic P fractionation. Scheme I is better than scheme II only in a system where noncrystalline Al-P is absent.

CHAPTER 8
SUMMARY AND CONCLUSIONS

Wavellite was the most common phosphate mineral in Ultisols formed from phosphatic materials of northern Florida, indicating the presence of wavellite under highly weathered soil conditions. Carbonate-fluorapatite and crandallite were restricted to pedons or horizons with relatively low eluviation, high base saturation, high extractable Ca and low KCl-extractable Al, such as in poorly to somewhat poorly drained soils.

Smectite was found in soils with carbonate-fluorapatite and wavellite; kaolinite in soils with crandallite and wavellite; and hydroxy-interlayered vermiculite in soils with wavellite.

Wavellite content in clays and silts increased with depth to a greater extent than did kaolinite content, indicating that wavellite is less stable in highly-leached, near-surface, soil environments.

The amount of P in wavellite was only a fraction of the total-P, indicating the presence of a significant adsorbed or non-crystalline constituent. The wavellite-P/total-P ratio was greater for B horizons than for A horizons.

The presence of noncrystalline phosphates in the phosphatic soils was inferred by low wavellite-P/total P or carbonate-fluorapatite-P/total P ratios but high oxalate-P/total P ratios. The noncrystalline Ca-P was extractable by oxalate but not by DCB. Both oxalate and DCB extracted noncrystalline Fe- or Al-P, but DCB is more effective in removing P associated with Fe.

Both Olsen- and Mehlich I-extractable P varied in phosphatic soils. The difference in P extractability was due to the presence of different amounts and kinds of crystalline and noncrystalline P. The Olsen-P and Mehlich I-P had linear functions with oxalate-P from the soils containing wavellite. Both Olsen P and Mehlich I-P were higher in Btg1 or B/E horizons as compared to the underlying horizons. The high extractable P in the B/E or Btg1 horizons was due to the presence of higher poorly crystalline Fe- and Al-P materials indicating higher availability of noncrystalline P than the crystalline P minerals.

Crystalline Fe or Fe-P minerals were not detected in the phosphatic soils although the DCB-Fe was relative high. In contrast, goethite was detected in the non-phosphatic soils. The oxalate-extractable Fe and P of both phosphatic and non-phosphatic soils showed a linear relationship suggesting that P in the phosphatic soils may have had an adverse effect in crystalline Fe oxide or hydroxide formation. Water content of the synthetic noncrystalline Fe-

P (initial pH 12.0) was lower than that of the synthetic goethite indicating replacement of the phosphate ion for hydroxyl ion or water. Phosphates associated with Fe were in poorly crystalline forms and were extractable to a large extent by Mehlich I and Olsen extractants.

Carbonate-fluorapatite was more soluble than wavellite by water, formic acid, oxalic acid, and citric acid at pH 3.0, 4.0, and 5.0. The effects of acid on solubility of carbonate-fluorapatite and wavellite decreased in the order, oxalic > citric > formic > water. Solubility of P minerals decreased more rapidly with pH increase in formic acid solution than in citric acid and oxalic acid solutions. Soluble P from carbonate-fluorapatite and wavellite reached relatively constant levels at one wk incubation at both concentrations of formic acid solutions ($3x10^{-2}$ and $3x10^{-3}$ M) and at the lower concentration of oxalic acid solution ($1.5x10^{-3}$ M). At the higher concentration of oxalic acid solution ($1.5x10^{-2}$ M) and both concentrations of citric acid (10^{-2} and 10^{-3} M), soluble P increased with time after one wk. The solubility of P minerals by oxalic and citric acids decreased when clay minerals were present due to neutralization of acidity and probably direct interactions between organic acids and clay minerals. But in water suspensions at initial pH of 4.0, which contained very low soluble P, vermiculite and montmorillonite tend to maintain soluble P at > 2 cmol m^{-3} level. Results suggested that

organic acids in soil can dissolve P from carbonate-fluorapatite and wavellite, especially at low pH values.

DCB extracted Fe-P and RS-P, but had little effect on crystalline Al-P (variscite and wavellite) and Ca-P (carbonate-fluorapatite); however, DCB is poor in differentiating Fe-P from Al-P because it extracted a considerable amount of both Fe-Al-P and noncrystalline Al-P. The extractability of crystalline Al-P by NH_4F depended on the mineral species. More P was extracted from the synthesized Al-P and wavellite than from variscite. A considerable amount of P from carbonate-fluorapatite was extracted by NH_4F, probably, by formation of CaF_2. More Al-P was extracted by NaOH than by NH_4F, but the reverse was true for carbonate-fluorapatite-P. Crandallite, an Al-Ca-P mineral, was only slightly dissolved by DCB, NH_4F, NaOH, and H_2SO_4.

The DCB, NaOH, and H_2SO_4 were used to extract Fe-P, Al-P, and Ca-P, respectively, in scheme I; but in scheme II, NH_4F, NaOH, DCB, and H_2SO_4 were used to extract Al-P, Fe-P, RS-P, and Ca-P, respectively. Phosphate in silt and clay fractions of Ocilla variant and Lochloosa variant was not completely removed by the sequential extractions of both schemes, indicating the presence of more resistant P material rather than simple Fe-P, Al-P, or Ca-P mineral forms. Scheme I underestimated Al-P and overestimated Fe-P since DCB dissolved noncrystalline Al-P. Scheme II also

underestimated Al-P and overestimate Fe-P since NH_4F did not remove all Al-P which was subsequently released by NaOH. The Ca-P in scheme II was underestimated because NH_4F extracted Ca-P to some extent. Therefore, both schemes are unsatisfactory in fractionating soil inorganic P. Scheme I is better than scheme II only in soil where noncrystalline Al-P is absent.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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